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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
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TECHNICAL PROGRESS REVIEWS

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Reactor Fuel Processing is a Technical Progress Review prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published in this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, G. Bennett, L. Burris, Jr., P. Fineman, A. A. Jonke, G. Kesser, S. Lawroski, W. J. Mecham, P. Nelson, D. Paige, J. Royal, J. Simmons, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

Section I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

By W. J. Mecham and A. A. Jonke

Fuel-Processing Plans

The Vitro Engineering Co. is making a study of a proposal to build a food-irradiation plant at Hanford near Richland, Wash. The announcement of the study cited the broad industrialization program in the Hanford area developed under AEC guidance.[1]

The Allied Chemical Corp. has established a nuclear fuels department in the company's General Chemical Division. The new department consolidates the company's nuclear energy activities, which include the fluoride-volatility plant at Metropolis, Ill., for production of UF_6 and the company's interests in chemical reprocessing and gas-centrifuge development.[2] The UF_6 plant at Metropolis is expected to reopen in 1966. The market in the next few years will depend on foreign requirements through ad hoc barter arrangements. At about the time of the start of toll enriching in 1969, a sizable market is expected[3] for the production of UF_6.

The AEC has granted a license to the General Electric Company for gas-centrifuge experiments. The company plans to conduct the experiments at its San Jose, Calif., installation.[4]

The Isochem Inc. Fission Products Conversion and Encapsulation plant at Hanford is expected to go into operation in 1968. To s imulate a market for ^{90}Sr, ^{147}Pm, ^{144}Ce, and ^{137}Cs, which will be produced at the Isochem Inc. plant, AEC has sharply revised downward the prices of these isotopes. The new prices are:

Strontium-90:
The price was $2 per curie. It now is 50 cents per curie for quantities up to 50,000 curies and 20 cents per curie for larger quantities.

Promethium-147:
The price was $5 per curie for quantities up to 20,000 curies. It now is 50 cents per curie for quantities up to 5000 curies and as low as 20 cents per curie for orders of more than 150,000 curies.

Cerium-144:
The price was $2 per curie for quantities up to 20,000 curies. The new price is 50 cents for orders up to 5000 curies. For very large quantities—more than 150,000 curies—it is 15 cents per curie.

Cesium-137:
Formerly $1 per curie for quantities up to 20,000 curies, the price now is 50 cents per curie for orders up to 10,000 curies, falling to 12.5 cents per curie for quantities above 200,000 curies.

Isochem Inc. is said to expect to supply the isotopes at even lower prices.[5] The AEC will discontinue the routine supply of these isotopes after the Isochem Inc. plant comes into operation.

A low-level-waste burial site for Illinois is to be operated by California Nuclear, Inc., of Lafayette, Ind.; the company was selected by the Illinois State Department of Health. The unspecified Illinois waste-disposal site will be the first in the Midwest. In taking this decision, the Illinois Department of Health cited Commonwealth Edison's plans to build two additional reactors on the Dresden I site and the possibility that a chemical reprocessing plant will be built in Illinois.[5a]

Both General Electric and Allied Chemical have announced plans for commercial-scale reprocessing plants, each with a capacity of about 300 tons/year, for operation in 1970. It is said that both are thinking only of sites east of the Mississippi and have indicated that they intend to use a combination of conventional aqueous technology and fluid-bed fluoride-volatility technology.[5b]

AEC Revises Specifications for Uranium Hexafluoride

The AEC has published a notice in the *Federal Register* revising chemical and physi-

Table I-1 SPECIFICATIONS FOR UF_6 DELIVERED TO AEC[7]

Item*	Numerical value
Max. vapor pressure of filled container at 200°F, psia	75
Min. UF_6 in material, wt.%	99.5
Max. hydrocarbons, chlorocarbons, and partially substituted halohydrocarbons, mole %	0.01
Max. number of parts of elements indicated per million parts of total uranium	
Antimony	1
Bromine	5
Chlorine	100
Niobium	1
Phosphorus	50
Ruthenium	1
Silicon	100
Tantalum	1
Titanium	1
Total of elements forming nonvolatile fluorides (having a vapor pressure of 1 atm or less at 300°C) e.g., aluminum, barium, bismuth, cadmium, calcium, chromium, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, silver, sodium, strontium, thorium, tin, zinc, and zirconium	300
Max. number of parts of elements or isotopes indicated per million parts of ^{235}U	
Chromium	1500
Molybdenum	200
Tungsten	200
Vanadium	200
Uranium-233	†
Uranium-232	†
Max. thermal-neutron absorption of total impurity elements as equivalent parts of boron per million parts of total uranium	8
Max. total of gamma activity due to fission products and ^{237}U as percent of gamma activity of aged natural uranium and as measured in a high-pressure ionization chamber	20
Max. beta activity due to fission products as percent of beta activity of aged natural uranium	10
Max. number of parts of plutonium per billion parts of total uranium	1
Max. alpha activity from all transuranic elements in disintegrations per minute per gram of total uranium	†

*All specification analyses on UF_6 are to be performed on samples removed in the liquid state from each cylinder while its contents are liquid and homogeneous.

†Because of interference of the gamma rays from ^{233}U and ^{232}U and their decay products with the use of existing monitoring equipment in the diffusion plants, the figures in the table would be 90 for ^{233}U and 0.011 for ^{232}U in parts per million parts of ^{235}U if such concentrations, resulting from high irradiation levels in reactors, were present in all the feed to the diffusion plants. Similarly the isotope ^{238}Pu and other transuranic elements resulting from high irradiation levels in reactors, if present in all the feed to the diffusion plants, would require a specification of 150 disintegrations per minute per gram of total uranium for the maximum alpha activity from such transuranic elements, for protection against health hazards in the maintenance of existing equipment in the diffusion plants. These matters are under study with a view to future establishment of specifications for ^{233}U and ^{232}U concentrations and for alpha activity taking account of expected feeds to the diffusion plants and of possible changes in equipment and procedures.

cal specifications for uranium hexafluoride (UF_6), the form in which uranium is enriched in the isotope ^{235}U in the gaseous diffusion plants.

Previous notices in the *Federal Register* have given specifications only for depleted or enriched uranium furnished by AEC or enriched uranium returned to AEC. The new notice provides specifications for all UF_6 delivered to AEC, regardless of ^{235}U assay, and applies to normal uranium as UF_6 to be supplied to AEC under ad hoc barter or toll enrichment arrangements. The new notice makes one change in specifications for enriched uranium, namely, to increase the minimum weight percent of UF_6 in such material from 99.0 to 99.5%.

The new notice also takes account of the fact that the ^{235}U assay assigned to normal uranium was previously changed from 0.7115 to 0.711% and accordingly sets a value of $23.46 instead of the former value of $23.50 per kilogram of uranium contained in normal UF_6 (Ref. 6). The new specifications are listed in Table I-1.

Economics of the Fuel Cycle

AEC Says Statutory Finding of Practical Value Must Await Adequate Demonstration of Large Water Reactors

The AEC announced that, although the economic prospects for nuclear power in the United States are very favorable, a statutory finding of practical value for light-water reactors must await an adequate appraisal of the economics, based on a demonstration of the technology and plant performance of large nuclear power plants now under construction. The essential economic test is the competitiveness of the nuclear plant with conventional power plants.

When a statutory finding of practical value is made for a type of nuclear power plant, the Commission then would license a facility of such type only under the commercial licensing section of the Atomic Energy Act. Licenses for power reactors built to date have been issued under the developmental licensing section of the law.[8]

Economics As a Basis of Burnup

The role of economic factors in fuel-cycle management was the subject of a paper presented to the Atomic Industrial Forum by Warren and McLeod.[9] After noting that fuel burnup has been identified as the single most important parameter in fuel costs, the authors listed fuel fabrication, shipping, reprocessing, and all fuel lease- and working-capital interest charges as cost components that vary inversely with burnup. These cost components make up about 55% of first-core and 45% of second-core fuel costs presently incurred by large water reactors. An economically optimum burnup was referred to as one beyond which added uranium-inventory costs more than offset additional reductions in those cost components which vary inversely with burnup. Thus the burnup specification of desired nuclear fuel performance appears to be determined most importantly by economic and utility-system characteristics.[9]

Economic Evaluations Under Way for Oxide-Fuel Fabrication

The status of continuing evaluations of fabrication of PuO_2-UO_2 fuels for use in thermal reactors was reviewed from an economic viewpoint by Biancheria and Allio.[10] The authors consider that strong economic incentives exist for the reinsertion of plutonium in commercial oxide-fueled thermal reactors even though the cost of fabricating plutonium-bearing fuel is more than 10% higher than for fabricating uranium alone.

Pelletizing and vibratory compaction are the processes most highly developed and economically promising. The comparisons between these processes are considered in detail as to the different technical features and the economic implications of these differences. The authors state that early assumptions as to relative cost effects of cladding and density for the two processes have had to be reexamined with new data obtained in continuing developmental work. For example, although the dimensional tolerances are lower for tubing (cladding) in the case of vibrationally compacted fuel, the vibration process itself imposes special requirements on tubing that may entail more stringent specifications on crack depth and length.

The authors briefly comment on preparation of PuO_2-UO_2 mixtures. Dry mechanical blending of the separate oxides as powders is considered to provide adequate mixtures at lower cost than coprecipitation from a mixed solution. However, the authors did not evaluate the possible role of alternative methods of synthesis of oxide, which yield directly particles of higher density than conventional wet methods. Such new methods under development are the sol-gel process and the fluid-bed process for preparation of UO_2 from UF_6.

Other points of comparison for fuel prepared by the two methods of fabrication included final fuel density, thermal conductivity of oxide, thermal contact with cladding of various shapes, gas absorption during preparation, fuel swelling, fission-product gas release during irradiation, and accommodation of released gas in the voids volume. The authors consider that some previous estimates have exaggerated cost differentials between vibrationally compacted fuel and pelletized fuel. From a present view of overall economics, the cost differential was estimated to be less than 5%.

After a discussion of irradiation testing programs of PuO_2-UO_2 fuels, it was concluded that "both vibrationally compacted and pelletized fuel rods are reliable for use in thermal reactors of present design, provided proper quality control is exercised during manufacture."[10]

Cost Penalties for Remote Fabrication of Nuclear Fuel

The total cost of producing heat or power by nuclear energy is composed of a multitude of interacting relations. Continuing studies are being made of fabrication costs to facilitate cost comparisons for alternative sets of fuel-cycle requirements and restrictions. One study at Oak Ridge National Laboratory has the aim of developing computer programs for the calculation of fabrication costs for various assumed fuel specifications. Programs are written for combination systems of specified design of fuel element, fuel material, fabrication process, and type of core-to-cladding bonding. Metal-, oxide-, and carbide-fuel types are represented among the programs presently available.[11]

Recently, refinements have been introduced into the programs which allow the calculation of shielding required in remote and semi-remote plants and the assessment of the economic penalties associated with the shielding. Detailed calculations have been made of the

shielding requirements and total fabrication costs in conceptual plants for the fabrication of certain ^{233}U-bearing fuels of the carbide type, namely, fuel for the Spectral-Shift Control Reactor (SSCR) and an advanced high-temperature gas-cooled reactor. The conceptual plants were of capacities between 60 and 3700 kg/day, operating three shifts per day for 260 days of the year and producing only a single type of fuel.

For the various containment requirements for SSCR fuel fabrication, four alternative modes of fabrication were used. These modes (in order of increasing cost) are: hooded, glove box, semiremote, and remote. The fabrication cost as a function of plant capacity for the SSCR fuel is illustrated in Fig. I-1. For the

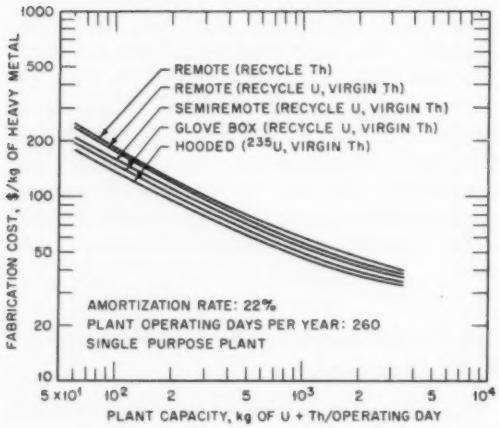

Fig. I-1 Effects of production rate and mode of fabrication on the cost of fabricating SSCR fuel elements.[11]

range of throughputs from 100 to 1000 kg/day, the unit cost of the highest cost mode of fabrication would be about 32% greater than that of the lowest cost mode. For the lowest cost (hooded) mode of fabrication, the unit cost would range from about $140/kg at 100 kg/day capacity to $48/kg at 1000 kg/day capacity.

In this study, semiremote fabrication would be used for fuel containing no more than 5 ppm ^{232}U, which has shielding requirements of 0.8 to 3.5 in. of steel. Remote fabrication facilities would have shielding requirements of 12 to 43 in. of concrete for fuels with concentrations of ^{233}U of about 5 ppm and higher.[11] (The radiation corresponding to various concentrations of ^{233}U was reported previously in *Nuclear Safety*.[12])

Review of Nuclear Industry 1965

A comprehensive review of the nuclear industry in 1965 has been made in a publication by the AEC Division of Industrial Participation. Feed-material processing, uranium enrichment, fuel fabrication, fuel reprocessing, and waste disposal are topics discussed.[13]

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Fluid-bed and pressurized aqueous combustion processes for graphite-matrix fuels are described. Shear–leach, electrolytic decladding, and sulfuric acid preparation of oxide fuels are also discussed. New amine and phosphate ester solvent processes appear to be practical, and studies of the behavior of ruthenium in solvent extraction continue to be of interest.

Preparation for Fuel Processing

By C. E. Stevenson

Graphite-matrix fuels may be prepared for processing by burning them in a fluidized bed or by oxidation in HNO_3 at high pressures. Sulfuric acid decladding of UO_2-PuO_2 mixed oxide fuels is unsatisfactory because of high losses of uranium and plutonium, but sheared fuel is readily dissolved in HNO_3 without the addition of fluoride. Uranium is readily leached by HNO_3 from the residue left by fluid-bed decladding of stainless-steel-clad UO_2 with $HF-O_2$ at 600°C. An alloy of uranium–2% zirconium has been dissolved satisfactorily for processing in 6.6*M* HF along with zirconium containing a small amount of uranium. Protactinium is effectively scavenged from $Th(NO_3)_4$ solutions by precipitation of MnO_2.

Treatment of Graphite-Matrix Fuels

The resistance of graphite to chemical attack greatly complicates the recovery of uranium from graphite-matrix fuels in which the uranium is probably contained as carbide particles after exposure to high temperatures. Methods for the preparation of such fuels for solvent-extraction-recovery processing have included ashing, grinding, and acid attack. In recent work at Oak Ridge National Laboratory (ORNL),[1] burning of the graphite in a fluidized bed of Al_2O_3, followed by leaching in boiling HNO_3, and submerged combustion in oxygenated dilute HNO_3 at 300°C have been studied as methods for the preparation of graphite fuels.

In the fluid-bed process, oxygen is used for combustion to minimize off-gas problems. Graphite compacts containing thorium and uranium, similar to those planned for the Peach Bottom High Temperature Gas Cooled Reactor (HTGR), were crushed to about $\frac{1}{8}$ in. in diameter and fed to a 2-in.-diameter bed of 60- to 90-mesh Al_2O_3 at 750 to 775°C. A free-flowing, finely divided ThO_2-UO_2 ash was produced, which was 99.7% dissolved in 7 hr in 13*M* $HNO_3-0.04M$ HF–0.1*M* Al^{3+} (Thorex dissolving reagent). Pilot-plant work is also being undertaken at the Idaho Chemical Processing Plant on this process using coated-particle elements containing only uranium.[2] An initial burning and ash-leaching test has been completed.

In the other process studied,[1] called Pressurized Aqueous Combustion (PAC), 500-μ HTGR fuel particles (12% thorium, 6% uranium, 82% carbon) with a pyrolytic carbon coating were reacted for 24 hr in an autoclave at 300°C in the presence of oxygen. System pressures at this temperature were of the order of 1500 to 2000 psi. Complete combustion of the carbon was achieved to produce an off-gas consisting mainly of CO_2 and O_2, and little or no HNO_3 was converted to nitrogen oxides. The uranium and thorium present were completely solubilized only when the $NO_3/(Th + U)$ mole ratio was greater than 50. This was attributed to the strong tendency of $Th(NO_3)_4$ solutions to hydrolyze at elevated temperatures. The pyrolytic carbon coatings were oxidized much more slowly than the graphite-particle base. Cor-

rosion of the autoclave appears to be a significant problem.

Graphite oxidation was also studied in a flow system. In this system, it was determined that oxidation rates increased in proportion to HNO_3 concentration, temperature, and surface area of the graphite. Agitation was also effective in accelerating oxidation.

Preparation of Stainless-Steel-Clad PuO_2–UO_2 Fuel

The processing of mixed-oxide fuels (PuO_2–UO_2) will become increasingly important to the nuclear industry as the utilization of plutonium in both fast breeder and thermal reactors is increased. Several recent reports have been concerned with the preparation of such fuels for the recovery of fissionable material. Stainless steel is a typical cladding material for mixed oxides, and means for its dissolution or removal are required.

In a report[3] by Goode at Oak Ridge National Laboratory (ORNL), H_2SO_4 decladding–HNO_3 dissolution is compared with shearing and HNO_3 leaching for the preparation of fuel solutions from stainless-steel-clad, swaged or pelleted 20% PuO_2–80% UO_2 prototype fuel for fast breeder reactors. Burnup of the 27 specimens used, all of which had been sectioned to expose the fuel for examination, ranged from 9000 to 99,000 Mwd/metric ton and averaged about 50,000 Mwd/metric ton. Removal of the cladding with boiling $6N$ H_2SO_4 resulted in the dissolution of 0.2 to 4.3% of the uranium and 0.2 to 4.5% of the plutonium. The percentage of material lost correlated neither with the burnup nor with the method of compaction, and the loss was thought to be too great for satisfactory economic utilization of this decladding method. In addition, the decladding solution was found to contain 11 to 94% (averaging 60%) of the ^{137}Cs initially in the fuel. It was believed that this would materially increase the cost of waste disposal.

The PuO_2–UO_2 cores, both from the specimens that had been declad with H_2SO_4 and from other specimens that had not been declad, dissolved readily in $3.5M$ to $10M$ HNO_3 in about 5 hr. The latter specimens simulated the sheared fuel that would be fed to the leaching step of a shear–leach head-end process. The rate of dissolution appeared to be several times greater than that for unirradiated mixed oxide. Contrary to experience with PuO_2 alone, the presence of fluoride was found to be unnecessary for rapid dissolution of mixed oxide. This behavior was attributed to the presence of a solid solution of PuO_2 in UO_2. On leaching a clad specimen, the ORNL workers found only 0.13% of the uranium and plutonium in an insoluble residue. The fission products, except for small amounts of molybdenum, zirconium, palladium, and rhodium, also dissolved in the HNO_3. Since these fission products from high-burnup fuels may amount to 2 to 3% of the core weight, it was believed that their removal from the fuel solution would be necessary before reprocessing by solvent extraction or ion exchange could be undertaken.

In other work at ORNL,[1] studies were made of the leaching of U_3O_8 from a mixture of Al_2O_3 and stainless-steel oxides produced by decladding stainless-steel-clad UO_2 in a fluidized bed of Al_2O_3 by treatment with 40% HF–60% O_2 at 600°C. This decladding treatment, believed to be equally applicable to UO_2–PuO_2 mixtures, produced a decladding product in powder form which typically contained 25% U_3O_8, 13% stainless-steel compounds, 5% fluorine, and 67% Al_2O_3. Leaching the powder for 5 hr with boiling HNO_3 ($1M$ to $15M$) containing 0 to $1M$ $Al(NO_3)_3$ for corrosion control dissolved 99.6 to 99.9% of the uranium to produce a leach solution that was about $0.2M$ in uranium and $0.6M$ in fluoride; the HNO_3 solution dissolved only about 2% of the Al_2O_3. Since the presence of such a concentration of fluoride may result in equipment corrosion, a technique was developed to remove about 85% of the fluoride from the bed by pyrohydrolysis with steam or O_2–3% H_2O at 200 to 600°C for 3 hr.

A note in a report from Pacific Northwest Laboratory[4] indicates that high-fired UO_2–PuO_2 and PuO_2 may be dissolved slowly (4 mils/day) in 75% H_3PO_4 at 120°C. This reagent was reported not to be excessively corrosive to type 304 stainless steel. A literature review on the dissolution of PuO_2 has also appeared.[5]

Dissolution of Uranium–Zirconium Alloy

The third core used in the first Experimental Breeder Reactor (EBR-I) consisted of an alloy of highly enriched uranium with 2% zirconium, coextruded with Zircaloy-2 clad-

ding. The uranium was recently recovered from the irradiated core alloy at the Idaho Chemical Processing Plant,[2] in conjunction with the processing of high-zirconium-alloy fuel of the Pressurized Water Reactor (PWR) seed type, in which the uranium-to-zirconium ratio is roughly the inverse of that in the EBR-I fuel. The process initially involved continuous dissolution[6] of the PWR type fuel in 6.6*M* HF, with the addition to the dissolver of a minor amount of the EBR-I fuel (2 kg per 600 kg of zirconium alloy). The zirconium content was maintained on the basis of keeping the sparingly soluble UF_4 in solution. As in the normal zirconium process, $Al(NO_3)_3$–HNO_3 was added to the dissolver solution to permit tributyl phosphate (TBP) extraction. Since it was suspected that the EBR-I fuel might be accumulating in the dissolver, this procedure was changed to provide for its separate dissolution. Separate dissolution was then effected in 6*M* HNO_3–0.75*M* HF in a Carpenter-20 dissolver, and the resulting solution was then blended with the adjusted dissolver product from dissolution of the PWR type fuel for subsequent extraction. Although the joint operation prevented appraisal of the processing effectiveness on the EBR-I material, overall recovery and decontamination appeared to be satisfactory.

Separation of Protactinium from Irradiated Thorium

The separation of 20,000 curies of ^{233}Pa from irradiated ^{232}Th by scavenging with MnO_2 from a HNO_3 solution was recently described.[7] This operation was carried out on a hot-laboratory scale at the Materials Testing Reactor (MTR). Recent reports from both Hanford Atomic Products Operation and Savannah River Laboratory have considered the plant-scale application of this technique.

Humphreys of the Pacific Northwest Laboratory described hot-cell studies on MnO_2 coprecipitation of ^{233}Pa as a head-end operation for Thorex processing in the Purex facility.[8] In initial studies the MnO_2 scavenging was carried out in a 0.1*M* acid-deficient, 1*M* $Th(NO_3)_4$ solution, produced by dissolver boildown. However, with only 0.1 mole of conformed MnO_2 per liter of solution, separation of protactinium was quite poor and was not improved with the addition of preformed MnO_2. With a greater precipitate volume, protactinium separation improved, but the quantity of precipitate (35% of the solution) became too large to handle. Good results (recovery of 97% of the protactinium at a loading of 10 mg of protactinium per gram of MnO_2) were obtained by coprecipitation of 3.5 g of MnO_2 per liter from an acidic feed solution (1*M* $Th(NO_3)_4$, 1*M* HNO_3, 0.01*M* HF) to which 0.1*M* sulfamic acid had been added to stabilize the precipitate against radiation decomposition.

The plant operation on six tons of irradiated thorium was successfully carried out by the use of 0.04 mole of coformed MnO_2 per liter of 1*M* $Th(NO_3)_4$. The recommended feed-solution composition was 1*M* HNO_3, 0.01*M* HF, 0.1*M* sulfamic acid, and less than 0.1*M* $Al(NO_3)_3$. The centrifuged MnO_2 was decomposed with sucrose at 70°C, precipitated sulfates were separated, and the protactinium was reprecipitated and concentrated by MnO_2 scavenging.

A Du Pont study[9] deals with semiworks tests of the MnO_2 precipitation and washing procedure in plant-scale equipment (a 40-in.-diameter 4-compartment Bird vertical centrifuge with a 60-gal dynamic volume). On the basis of laboratory data for the effective sorption of ^{233}Pa by MnO_2, a more dilute flow sheet than in the conventional Thorex process was used; the test feed solutions were about 0.4*M* $Th(NO_3)_4$, 0.4 to 0.8*M* HNO_3, and 0.7 to 0.8*M* $Al(NO_3)_3$ [the $Al(NO_3)_3$ results from acid dissolution of the thorium cladding]. No protactinium was utilized in the semiworks tests. Sulfamic acid was first added to decompose any HNO_2 present, which would otherwise redissolve some of the precipitated MnO_2. At least 1 mole of NH_2SO_3H was required per mole of NO_2^-. Workers accomplished the precipitation of about 60 lb of MnO_2 per 2700-gal centrifuge batch by adding $Mn(NO_3)_2$ to the dissolver solution at 70°C and then adding, at a slow rate, 85% of the stoichiometric amount of $KMnO_4$ required for conversion of all the manganous salt to MnO_2. Excess $KMnO_4$ was avoided to prevent oxidation and release fission-product ruthenium. The MnO_2 was centrifuged and washed five times with 50 gal of 0.1*M* HNO_3, slurried from the bowl and dissolved with $NaNO_2$ in acid solution, in order to yield high-purity ^{233}U by ^{233}Pa decay in storage.

In this connection a review of thorium-reprocessing methods has recently been issued by Roberts and others of ORNL.[10]

Solvent-Extraction Processes

By C. E. Stevenson

Limited extraction of nitrosylruthenium nitrato complexes indicates that dibutyl cellosolve (DBC) should be a good diluent for tertiary-amine solvents. The presence of nitroalkanes and carbonyl compounds in paraffinic diluents used in TBP processes is indicated. Plutonium may be extracted directly from a uranium–plutonium fuel solution in HNO_3 by extraction with Alamine 336 in DBC. In another process plutonium extracted by a tertiary amine is precipitated directly from the organic phase. Di-2-amyl 2-butyl phosphonate gives decontamination similar to that obtained with TBP in a Purex type process.

Ruthenium Decontamination in Extraction Processes

The formation of nitrato complexes from nitrosylruthenium enhances the extractability of this fission product and may lead to poor decontamination of fissionable materials in solvent-extraction systems. A series of reports on this subject has been provided by Scargill and others at Harwell, the last[11] of which was discussed in *Reactor Fuel Processing*, 9(1). A further report by Scargill, Lyon, and Wain[12] describes the relative extractability of the tri- and tetranitrato nitrosylruthenium complexes by dibutyl cellosolve (DBC) and by β,β'-dibutoxy diethyl ether (Butex). The behavior of DBC is of interest for use as a diluent for tertiary amines to alleviate the formation of a third phase when plutonium is extracted from HNO_3 solutions of irradiated fuels, and Butex is used as a process solvent in Great Britain.

DBC was found to be a relatively poor extractant for the tri- and tetranitrato complexes, particularly at low HNO_3 concentrations (at $3\,M$ HNO_3 in the aqueous phase, partition coefficients of 0.09 and 0.22 were observed for the tri- and the tetranitrato complexes, respectively, at 20°C). Therefore DBC should be a suitable tertiary-amine diluent, and its use should not result in poor ruthenium decontamination. Butex, however, extracts relatively more of the tri- and tetranitrato complexes than DBC (partition coefficients for $3\,M$ HNO_3 of 2.2 and 7, respectively, at 20°C). Furthermore, reaction kinetics in the Butex phase favor the formation of the most extractable tetranitrato complex from the trinitrato complex. This is reflected in a decontamination factor of only about 3, obtained for RuNO nitrato complexes in Butex countercurrent extraction processes.

Lloyd and Mason at the Massachusetts Institute of Technology have also conducted studies on the solvent-extraction behavior of nitrosylruthenium nitrato complexes in tertiary-dodecylamine systems. In a recent report[13] on studies utilizing the variation in distribution ratio on changing phase ratios, rates of hydrolysis of the less and more extractable species were given as $K_1 = \sim 0.01$/min and $K_2 = \sim 0.15$/min, respectively. An observation of a resistance of the less extractable species to transfer back to the aqueous phase was noted. This behavior leads to variations of distribution with time, as conversion of the less to the more extractable species occurs in the organic phase.

Difficulties in the preparation of a pure trinitrato nitrosylruthenium were also noted, and the presence of an anomaly in the extraction of the nitrato complexes was indicated. It was suggested that the less extractable trinitrato complex was probably extracted as follows:

$$RuNO(NO_3)_3 \cdot 2H_2O + R_3HNO_3 \rightleftharpoons R_3NH \cdot RuNO(NO_3)_4 \cdot H_2O + H_2O$$

and that the organic phase complex then undergoes further conversion by reaction with more amine

$$R_3NH \cdot RuNO(NO_3)_4 \cdot H_2O + R_3HNO_3 \rightleftharpoons (R_3NH)_2RuNO(NO_3)_5 + H_2O$$

The more extractable tetranitrato species is probably extracted as follows:

$$RuNO(NO_3)_4 \cdot H_2O + 2R_3NHNO_3 \rightleftharpoons (R_3NH)_2RuNO(NO_3)_5 + NO_3^- + H_2O$$

Thus the species that appears in the organic phase following extraction of the tetranitrato complex is the same as the species that results from the conversion of the extracted

trinitrato complex. This would explain why, after standing, the spectrum of the organic phase becomes independent of the species involved.

Diluent Selection and Degradation

The chemical and radiolytic degradation of hydrocarbon diluents used for TBP and related solvents for heavy metals are of major significance in process performance. The advantages of pure normal paraffinic hydrocarbons for this purpose have been noted previously, in particular as the results of studies at Savannah River.[14] The use of a commercial mixture of *n*-paraffins was initiated at Savannah River in 1961 for Purex-process operations. Generally, quite satisfactory diluent performance has been experienced since then, as reported by Marston, West, and Wilhite,[15] and, although considerable makeup solvent has been added, the same batch of material is still in use. The accumulation of degradation products, indicated by zirconium retention, gas chromatography, infrared absorption, and polarography, has been extremely low.

The nature of the changes in the diluent has been indicated best by gas chromatography and infrared spectrometry. Gas chromatograms showed an increase in average paraffin chain length, and the presence of some nonparaffin components was indicated. Infrared measurements showed increased absorbance at 6.4 μ, attributed to nitroalkanes, and at 5.8 μ, attributed to carbonyl compounds.

The overall solvent quality has generally been monitored by measurement of its relative retention of zirconium, or "Z" number. A simpler test, which was devised later, involved polarographic measurement of reducible species at - .1 volts. The diffusion current has been found to be proportional to the Z number.

The diluent-degradation products have not yet been specifically identified, but their concentration, as indicated by chromatography, suggests that they might now be isolated by gas and thin-layer chromatography. Subsequent identification of the fractions by infrared examination should then be feasible.

Studies of hydrocarbon-diluent degradation have also continued at ORNL.[1] Emphasis was placed on substituted aromatic diluents since these are of particular value in amine systems and for use with phosphorus-containing extractants other than TBP. The major degradation product of diethylbenzene, produced by HNO_3 in the presence or absence of radiation, was identified as 1-α-nitroethyl-4-ethylbenzene. A small amount of ethylbenzoic acid was also isolated. It was found, however, that addition of these compounds to pure diethylbenzene did not enhance the extraction of hafnium (analogous to zirconium) by TBP contained in the diluent. It was therefore concluded that degradation of impurities in diethylbenzene was responsible for adverse effects on extraction performance.

Amine Extraction Systems

At Harwell work is being carried out on the development of a simplified processing scheme for a hypothetical fast reactor fuel, which consists of 75% uranium–25% plutonium. The process involves solvent extraction of the plutonium with Alamine 336 in dibutyl cellosolve (DBC), the uranium being rejected to the raffinate. Solvent selection and distribution data have been discussed previously.[11] A recent report by Streeton and Holdoway describes some flow-sheet development studies using laboratory-scale mixer–settlers.[16] In most of the tests, U(IV) was used as a stand-in for plutonium, but one test with plutonium was carried out.

An operable flow sheet involved extracting the approximately 0.8*M* U(IV)–Pu(VI) nitrate solution (~1*M* HNO_3) with 4.8 volumes of 15% Alamine 336 in DBC and contacting the solvent with 1 volume of 1*M* HNO_3 scrub. The high solvent-to-feed ratio was necessary in order to avoid the formation of a third phase, and the solvent contained less plutonium than was desirable (10.5 g/liter). The plutonium was satisfactorily stripped from the solvent in 11 stages of the mixer–settler by the use of a backwash solution of 1*M* CH_3COOH–0.05*M* HNO_3. In studies with uranium and fission-product tracers, decontamination factors of only 42 for ruthenium and of 240 for zirconium–niobium were obtained. The ruthenium had been converted to the form of the nitrato nitrosylruthenium complexes, and the presence of 2.4% of the ruthenium in the form of the highly extractable tetranitrato species was indicated.

Trilaurylamine in dodecane has been used in the Marcoule plant for the concentration and decontamination of plutonium after its separa-

tion from uranium.[17] Development work on a plutonium-purification process with trilaurylamine (TLA) has also been carried out for the Eurochemic plant at Mol, Belgium. Rolandi, van Geel, and Geoffroy have recently described[18] an interesting variation in which, after extraction with 20% TLA in Solvesso-100, the plutonium is precipitated directly from the organic phase (containing 15 g of plutonium per liter) by mixing the latter with one-third its volume of 0.45*M* oxalic acid containing 1*M* HNO_3. After settling, the organic phase is decanted, and the suspended precipitate is washed with 1 volume of 2*M* HNO_3–0.02*M* oxalic acid. A decontamination factor of 50 to 100 and a loss of 0.02% plutonium were indicated for the precipitation step. Continuous precipitation and washing are planned.

Applications of Phosphonate Extractants

Some time ago it was noted that butyl phosphonate esters possessed significant potential advantages over TBP because of high extraction coefficients, greater radiation stability, and compatibility with aromatic diluents.[19] Schlea and Jennings of Savannah River have recently described[20] a test of a Purex type process in which the solvent used was 33 vol.% di-2-amyl 2-butyl phosphonate (DABP) in a hydrocarbon diluent, in place of 30 vol.% TBP. A one-cycle[21] test was conducted on a small scale using miniature centrifugal contactors with organic-phase residence times in each stage of 4 to 6 sec.

Stream compositions and flow rates were generally similar to those used for conventional Purex processing; however, a split-extraction flow sheet (part of the solvent is added at the uranium-saturated extraction stages) was used to prevent the refluxing of Pu(IV) or zirconium in the scrub stream, which would accompany refluxing of HNO_3 in the extraction section. Process performance was similar to that of a TBP Purex process in the same equipment (uranium decontamination factors of 4.1×10^4 for zirconium–niobium and 5.7×10^4 for ruthenium); a desired improvement in zirconium–niobium decontamination based on design data, however, was not realized. TBP-process decontamination factors were about 7×10^4 for zirconium–niobium and for ruthenium. The use of the short residence contactors also indicated that diffusion processes control transfer of actinides and most fission products in a manner similar to that occurring in conventional mixer–settlers.

Another and rather specialized application of a phosphonate extractant is described by Kingsley of Hanford.[22] Dibutylbutyl phosphonate (DBBP) (30 vol.% in CCl_4) was applied in a process developed for the recovery of americium from the aqueous waste. The waste resulted from TBP processing to recover plutonium from plutonium-bearing metallurgical scrap that had been stockpiled for several years. The waste solution contained 0*M* to 0.7*M* aluminum, magnesium, calcium, and iron in 2 to 4*M* HNO_3 and milligram quantities of plutonium and americium. The waste is partially neutralized (to 0.3*M* to 0.5*M* H^+) and extracted with an equal volume of solvent containing a small amount of HNO_3. The americium is stripped from the solvent with water to achieve an estimated 97% recovery.

Ion-Exchange Processes

By C. E. Stevenson

Vigorous exothermic reactions may result from the contact of anion-exchange resins used for plutonium sorption with warm oxidizing reagents (HNO_3, $Cr_2O_7^{2-}$). The kinetics of plutonium sorption follow Fick's diffusion law.

Thermal Effects in Ion Exchange

In recent years several fires have occurred in equipment used for recovery and concentration of plutonium by anion exchange.[23] In all cases the processing involved acidic nitrate solutions in confined units. Because of the obvious oxidizing ability of nitric acid and the oxidizability of organic-resin systems, an investigation was recently conducted at Hanford on thermal effects occurring in anion-exchange-resin–nitric acid systems[24] as related to pressurization, fire, and explosion. The findings of this investigation are discussed in detail in Sec. VI of this issue of *Reactor Fuel Processing*.

Plutonium Sorption Kinetics

A series of papers on plutonium ion exchange, written by James of Los Alamos Scien-

tific Laboratory, has been discussed previously.[25] The most recent contribution by James[26] describes the sorption kinetics of Dowex 1-X4 for Pu^{4+} from nitrate solutions. The particle-diffusion-controlled reaction appeared to proceed with an apparent average diffusion coefficient, which decreased exponentially with increasing plutonium sorption. Fick's law was found to apply. The trace–sorption diffusion coefficient depended strongly on aqueous-phase composition and was roughly proportional to the product of the corresponding distribution coefficient and the ratio of hydronium ion to water concentrations. An activation energy for diffusion of about 8.7 kcal/mole was estimated.

Plant and Equipment Design and Operation

By D. M. Paige

Operation of a pilot-plant electrolytic dissolver for stainless-steel cladding has been demonstrated. An integrated-cell concept has been developed for shear–leach processing.

Electrolytic Dissolution

With the increased interest in stainless steel for fuel cladding, it becomes desirable to develop a good reprocessing scheme for the removal of this cladding. Sulfuric acid and aqua regia systems have been considered in connection with standard extraction plants, and fused-salt volatility methods have been proposed. One of the more promising methods which integrates into existing aqueous processes is electrolytic dissolution using nitric acid. Progress along these lines has been reported in the review from time to time.[11,27]

Kerr, Lakey, and Denney, working at the Idaho Chemical Processing Plant, have written a report[28] covering extensive work done with a pilot-plant electrolytic dissolver. This report contains detailed information on equipment development, effects of variable dissolver capacity, dissolver development, and problems solved, as well as a proposed complete full-scale system for the Idaho Chemical Processing Plant.

Actual run data are reported for some 18 runs made in the Model 2 dissolver. Some of these runs have been described in the previous reviews; however, the following observations of interest were reported:

1. Average processing rates of approximately 1.05 g/hr per square centimeter of anode area could be expected with a current utilization of 0.66 g/amp-hr in some cases (higher than theoretical because of the multicell effect).

2. Fuel composition did not seem to affect dissolving rates, but smaller elements seemed to yield a higher current utilization (also multicell effect).

3. A partially filled dissolver gave lower current utilization, probably because of current bypassing. It was reported that improvements could be effected by the placement of an insulating plate in the unused portion of the dissolver.

4. The effect of dissolvent composition was mainly on the current flow because of solution conductivity. Maximum current was observed at 6.5*M* HNO_3 for pure acid, and at 3*M* acid having a metal concentration of 90 g/liter.

5. Higher temperatures increased solution conductivity but caused anode film resistance to increase. A temperature of 49°C was reported to be optimum in the Model 2 dissolver.

6. The pilot-plant power supply had a voltage range of 7 to 25 volts. Current density varied with voltage. Since no detrimental effects were noted up to 25 volts, it is suggested that a higher voltage might raise dissolver capacity.

7. Sludge (undissolved metal particles and siliceous compounds) coated surfaces, caused lower current densities, and, in one case, actually fouled the product cooler. Addition of gelatin (100 to 200 ppm in the acid feed) prevented sludge formation and allowed the particles to be circulated out of the dissolver. It was reported that these particles contained insignificant amounts of uranium.

8. Off-gas released was mainly composed of oxygen, nitrogen, and oxides of nitrogen. Hydrogen concentrations could be kept below hazardous levels by air dilution.

9. With the Model 2 dissolver as finally evolved, no corrosion problems were noted for the titanium vessel, the niobium basket, or the platinum anode.

The proposed plant-scale flow sheet is shown in Fig. II-1. The dissolver would, of course, be the only unusual piece of equipment and would

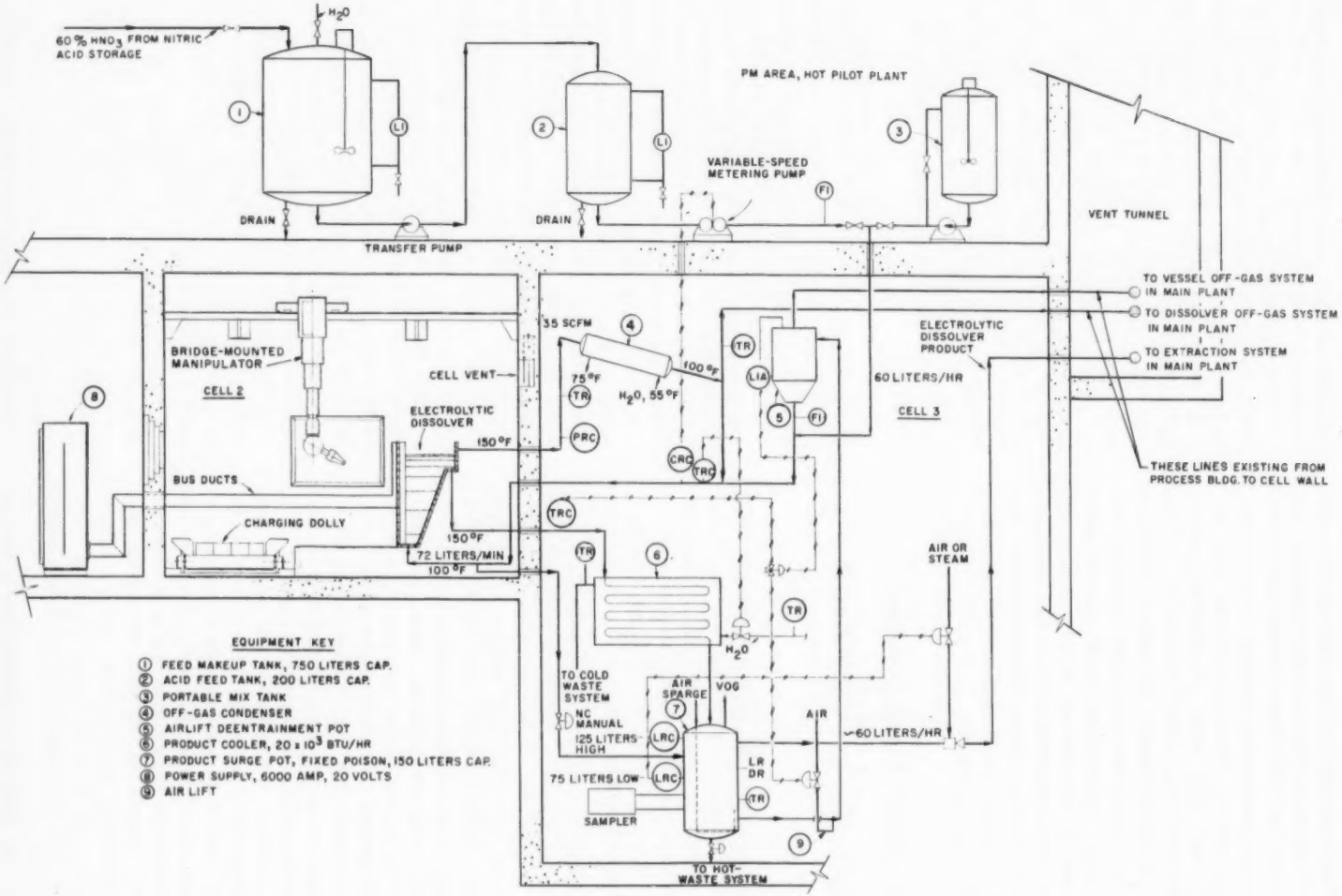

Fig. II-1 Flow sheet of conceptual plant-scale electrolytic-dissolution process installed in ICPP hot pilot plant.[28]

be similar to the Model 2 dissolver. Figure II-2 shows a cross section of the proposed dissolver. The length would be 80 in. to accommodate all proposed fuel shown in Table II-1.

Charging and maintenance of the dissolver would be accomplished by having it directly connected to a shielded cell with remote manipulators available.

Instruments would include:

1. An electromagnetic flowmeter in the recirculating product line.

2. A conductivity meter for the product solution entering the dissolver. The output of this meter and that of the dissolver density indicator would provide a continuous indication of the solution composition.

3. Temperature instrumentation for the solution entering and leaving the dissolver. One of these temperature points would control the water rate to the product cooler; the other would control the rate of flow of air supplied to the air lift.

4. Density instrumentation for the dissolver.

The primary instruments would be backed up by level instruments for the dissolver and overhead air-lift deentrainment pot and by temperature instruments at miscellaneous locations throughout the system.

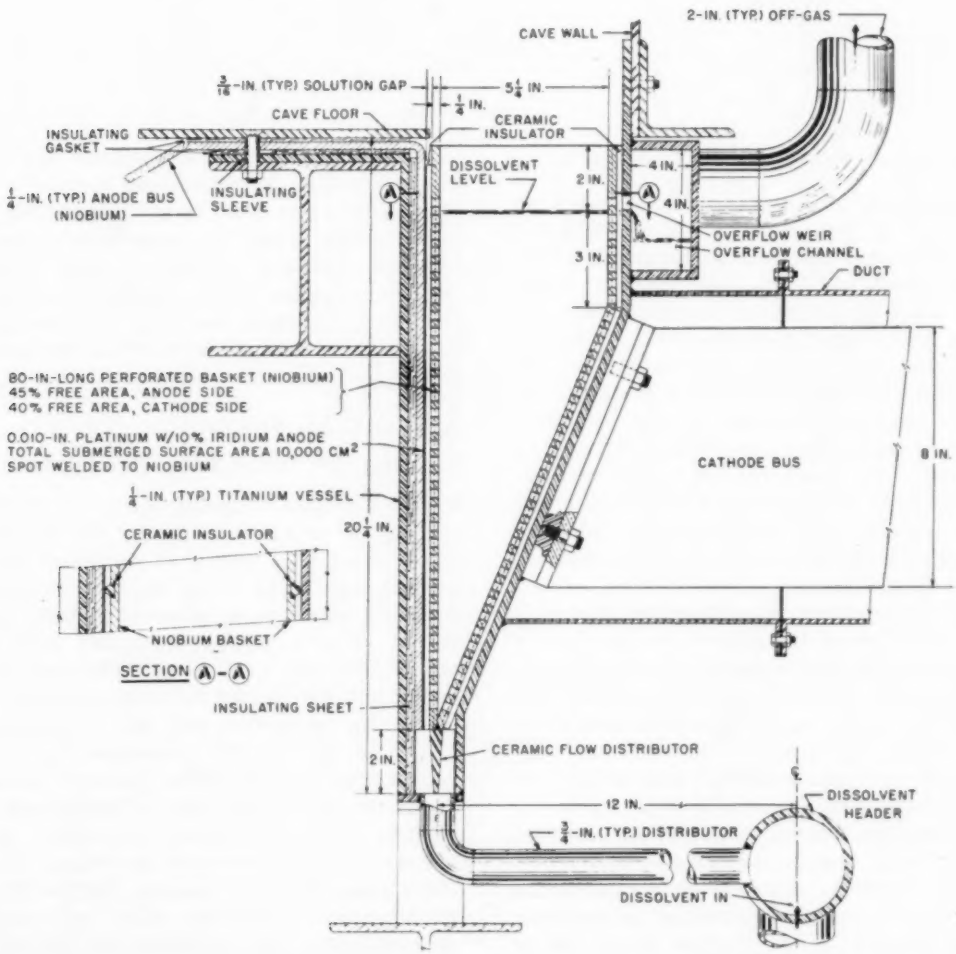

Fig. II-2 Cross section of conceptual plant-scale dissolver.[28]

The power supply would be rated at 10,000 amp at up to 30 volts, both controlled to ±1%.

The system would be geometrically safe, except for the product receiver, where the ^{235}U concentration would be kept below 12 g/liter by administrative control of the system.

cause no pressure surges when quenched in the dissolver.

Figure II-5 shows the batch leacher used in engineering-scale studies. Some tests have been run with sheared unirradiated stainless-steel-clad UO_2 and UO_2-ThO_2. In one test of

Table II-1 PHYSICAL CHARACTERISTICS OF FUELS CONSIDERED FOR REPROCESSING IN AN ELECTROLYTIC DISSOLUTION SYSTEM AT THE ICPP

Fuel	Shape	Outside dimensions
PM-1	Tube	0.506-in. OD by 33.5 in. long
PM-2A	Box of plates	2.863 by 2.863 by 27 in. long
PM-3A	Tube	0.506-in. OD by 33.5 in. long
SM-1 (APPR)	Box of plates	2.863 by 2.863 by 27 in. long
SM-1A	Box of plates	2.863 by 2.863 by 27 in. long
BORAX-V superheater	Box of plates	3.633 by 3.875 by 36 in. long*
NSP superheater	Tube	0.706-in. OD by 77.5 in. long
OMRE	Box of plates	2.8 by 2.9 by 40 in. long*
SPERT-III	Box of plates	2.95 by 2.95 by 38 in. long
VBWR	Box of plates	2.98 by 2.98 by 45 in. long*
HTRE	Concentric tubes	3.52-in. OD by 30 in. long

*After cutting off inert ends.

Shear–Leach Process-Cell Concept

A conceptual design has been prepared by ORNL[1] for an integrated cell to handle some of the corrosion-resistant stainless-steel-clad and Zircaloy-clad oxide fuels by use of the shear–leach equipment that was described previously in *Reactor Fuel Processing*.[29] Figure II-3 shows the process flow sheet for cell equipment, and Fig. II-4 shows the proposed cell in perspective. Most of the individual equipment items have been reviewed in detail previously, and there are only minor innovations involved in the proposed integrated plant.

The proposal of a cutoff wheel for removing hardware presents some possible explosion hazard from zirconium-particle fires, and wet cutting is, therefore, recommended. The handling of fuel from the chopper to the leacher was mocked up and demonstrated to be workable remotely. The fuel carrier is a perforated basket lined with a consumable liner of 10-mil-thick carbon steel. A Grayloc connector provides the seal between basket and leacher, and hinged Tube-Turn closures seal the top during transport. The leacher holds two fuel buckets in cylindrical vessels connected by a safe-slab tank for solution. Some detailed calculations are presented to demonstrate that heating from fission product in the baskets would not be a significant problem for fuel irradiated to 20,000 Mwd/ton and cooled 180 days and would dissolving UO_2, the time required was 2 hr. The consumable liner dissolved in about 2 min. The basket holds from 18 to 36 kg of fuel. The leached hulls would be monitored to ensure complete recovery of fuel by using delayed-neutron activation of the residual uranium and plutonium, a method that is sensitive enough to detect a loss of less than 0.01% of the fuel in a typical low-enrichment power-reactor fuel.

A Pilot-Scale Facility for Thorium Fuel-Cycle Development

The Thorium–Uranium Recycle Facility (TURF) at ORNL is designed for use in the development of a variety of processes for the several fuel types using the thorium cycle.[30] Sufficient shielding is provided to protect personnel from radiation emanating from fuel assemblies that have been irradiated to the levels now anticipated in power reactors. Although the equipment that can be installed in TURF is not of full production size, it is believed to be sufficiently production-like in design to allow collection of significant data relative to the economic evaluation of the various thorium fuel-cycle operations. The facility consists of four heavily shielded (5½-ft-thick normal concrete) cells, two shielded service cells, and an unshielded cell and air lock. (The cell layout is described in Ref. 30.) The unit is to be operated with an air atmo-

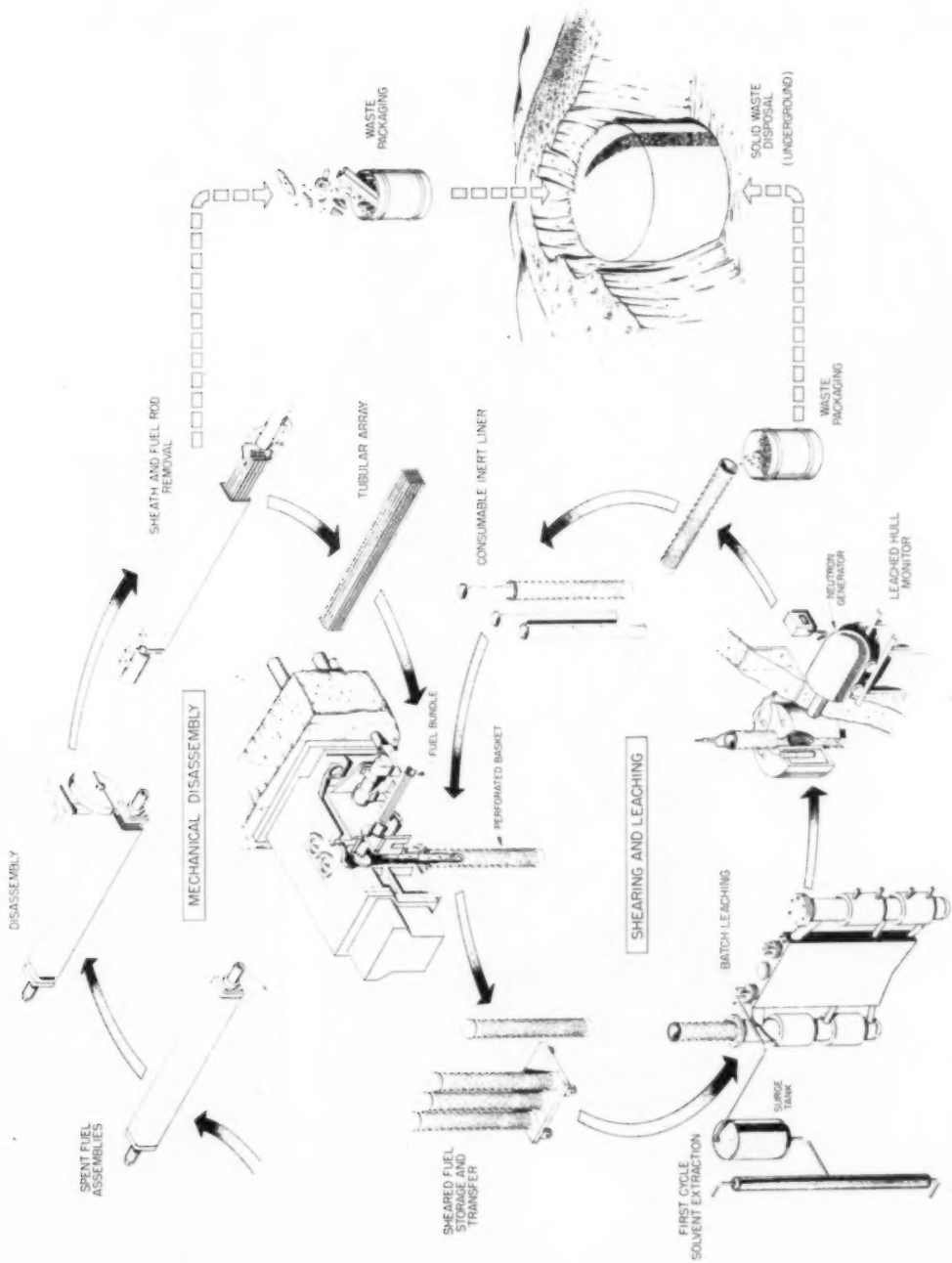

Fig. II-3 Flow sheet for shear–leach process for second-generation power-reactor fuels.[1]

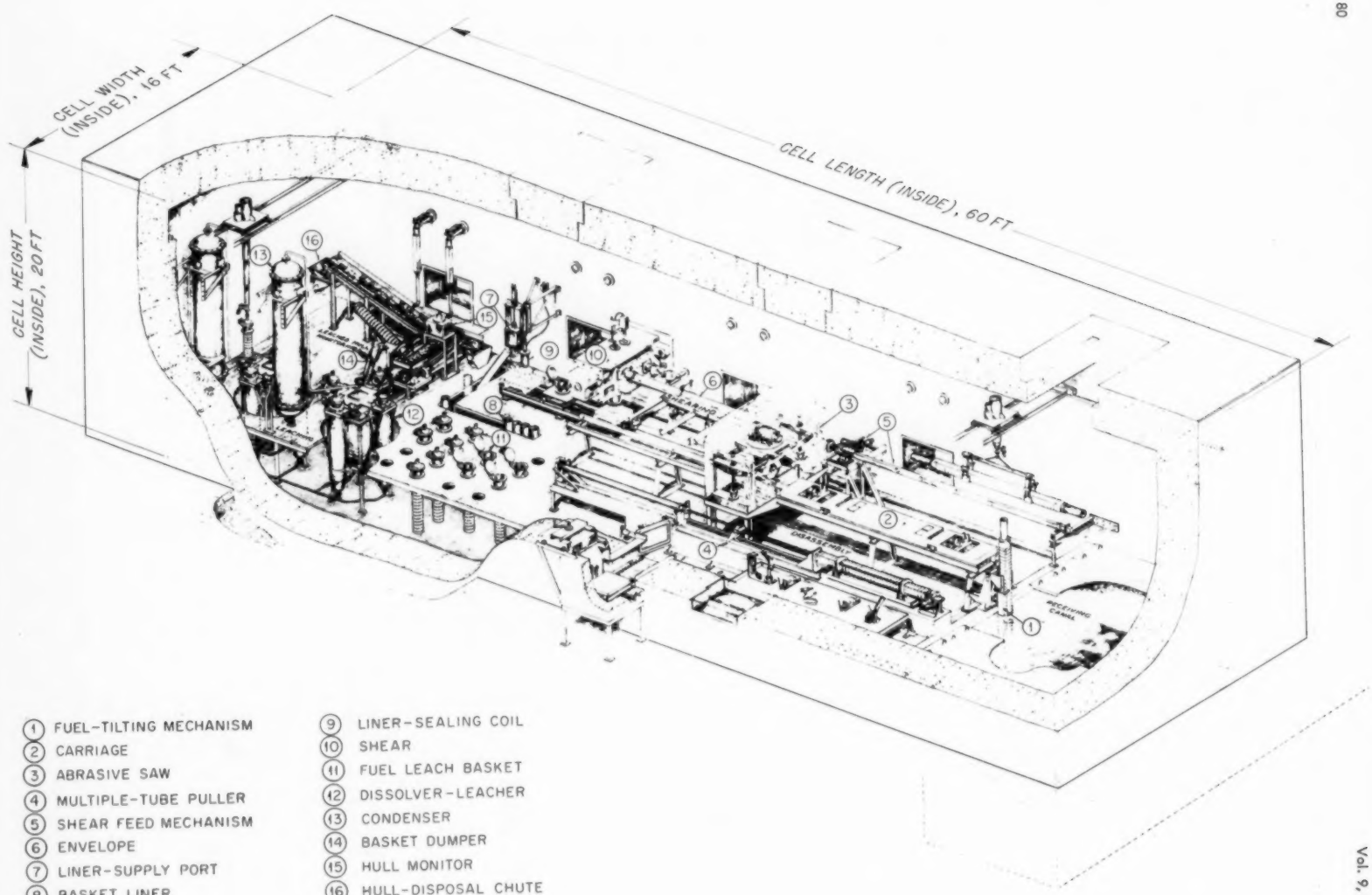

Fig. II-4 Optimized layout of equipment for the shear–leach process.[1]

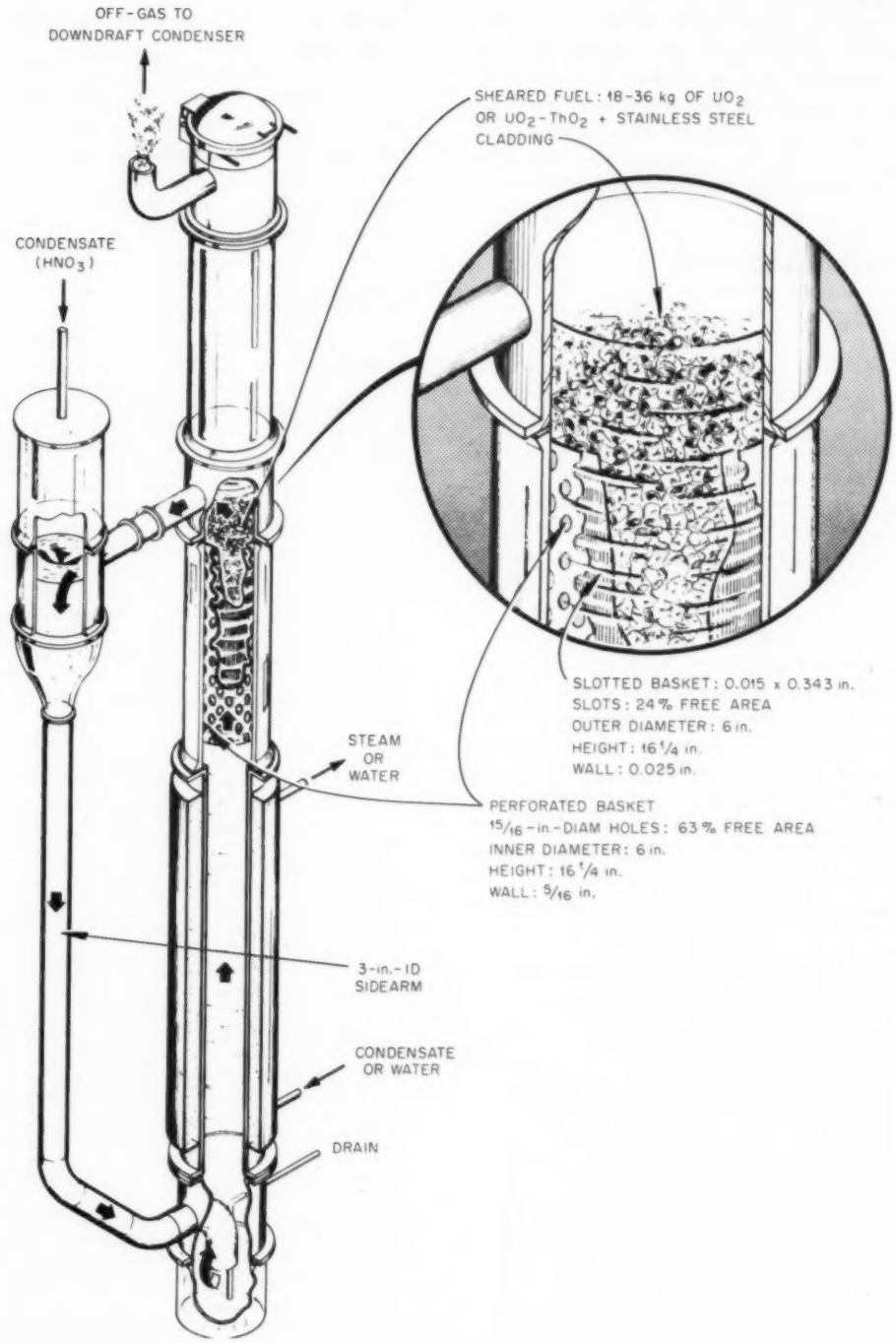

Fig. II-5 Engineering-scale 90-liter batch leacher for dissolving oxide fuel from sheared cladding.[1]

sphere initially and can be converted for operation with inert gas. Both remote and direct maintenance procedures are employed. The system utilizes in-cell cranes and electromechanical manipulators. Shielding windows are of two types: (1) lead glass and oil and (2) a composite of glass and zinc bromide. The facility is scheduled for completion in 1967.

Instrumentation

By D. M. Paige

With the refinement of various processes, it becomes increasingly desirable to monitor chemical compositions of process streams for the maintenance of satisfactory process conditions. Koski of Hanford reports[31] on the development of a device for the continuous and accurate measurement of the boiling point of a dissolver solution. Such data, along with specific gravity (easily measured), can be related to acid and uranium concentrations for the Redox dissolver solution.

Accurate boiling-point measurements require that vapor and liquid in thermal equilibrium be contacted with a temperature sensor. The device accomplishes this measurement by a modification of the Cottrell method. This method requires a sample pump, boiler equilibrator, and temperature-measuring system. The device works by heating a continuously obtained sample inside a 1-in. pipe and delivering it to a flashing chamber where temperature of the vapor–liquid mixture is measured with a resistance bulb as a sensor and recorded through a resistance bridge.

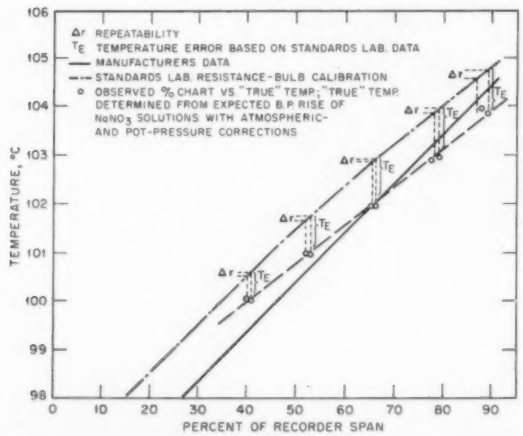

Fig. II-6 Boiling-point-monitor test results.[31]

Figure II-6 shows laboratory results of tests with the device. Koski concludes that a reproducibility of 0.1°C can be expected with a response time of 2 min. He further suggests that it would be necessary to calibrate a similar device if used with Redox or similar process solutions.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

By J. J. Barghusen

Volatility Processes for Uranium Carbide Fuels

OXIDATION–FLUORINATION PROCESS

Engineering-scale investigations on methods for processing graphite–uranium carbide fuels are being conducted at Brookhaven National Laboratory (BNL)[1] and Oak Ridge National Laboratory (ORNL).[2] These studies are applicable to the Rover Nuclear Rocket fuel, the High-Temperature Gas-Cooled Reactor (HTGR) fuel, and other fuels containing uranium carbide in a graphite matrix. The Rover fuel is composed of pyrolytic graphite-coated uranium dicarbide particles dispersed throughout a graphite matrix. Coolant channels within the graphite matrix are lined with niobium carbide.[3] The fuel for the HTGR is in the form of graphite cylinders containing pyrocarbon-coated microspheres of uranium–thorium dicarbide dispersed in a graphite matrix. The processing scheme for both fuel types consists basically in oxidation of the graphite and uranium carbide by oxygen to convert the graphite to CO and CO_2 and to convert uranium, niobium, thorium, and other materials to their respective oxides. The nonvolatile oxide ash is then treated by aqueous dissolution[2] or fluoride-volatility[1] techniques for the recovery of uranium.

A facility has been constructed at BNL[1] for demonstrating the fluid-bed oxidation–fluorination process with Rover fuel material. A description of the BNL facility and the result of demonstration tests were presented in a previous issue of *Reactor Fuel Processing*.[4]

In tests demonstrating the processing of Rover fuel material, it was observed that niobium was completely converted to volatile NbF_5 during fluorination and that this material accompanied the UF_6 in the off-gas from the fluorinator. Nearly complete separation of the two materials was achieved by the use of selective condensation and sorption techniques. A condenser maintained at 25°C was used to collect the bulk of the NbF_5. Less than 0.5% of the UF_6 was collected with the NbF_5 in this condenser. Any uncondensed NbF_5 was removed from the UF_6 gas stream by selective sorption on sodium fluoride at 400°C. The UF_6 passed unaffected through the sodium fluoride trap and was collected in a condenser at –50°C. The niobium concentration in the UF_6 product was generally less than 15 ppm.

In the oxidation of HTGR fuel material, the solid oxide appears as an intimate mixture of ThO_2 and U_3O_8. Fluorination of this material results in the formation of nonvolatile ThF_4 and volatile UF_6. Thus during fluorination a portion of the uranium might be occluded in the ThF_4 matrix. A series of experiments was performed in a 2-in.-diameter fluid-bed reactor to determine the fluorination conditions that would result in high uranium volatilization from oxidized HTGR fuel. Inert refractory alumina was used as the fluid-bed material. The fluorination sequence involved: 1 hr at 500°C with 50 vol.% fluorine, 1 hr at 525°C with 100 vol.% fluorine, and from 1 to 3 hr at 550°C with 100 vol.% fluorine. The application of this fluorination sequence led, in general, to unsatisfactory removal of uranium from the thorium–uranium oxide. Recycle of the alumina-bed material from a previous experiment was not satisfactory in reducing the retention of uranium; in both tests the recycled bed caked severely during fluorination. High uranium removal (>99%) was achieved by incorporation of an intermediate pyrohydrolysis step during fluorination. Figure III-1

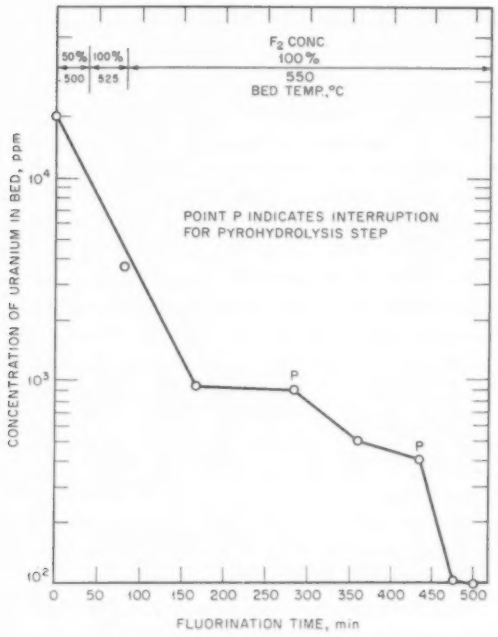


Fig. III-1 Recovery of uranium from HTGR fuel-oxidation products.[1] *[Reprinted, with permission, from* Industrial and Engineering Chemistry, Process Design and Development, *5(1): 51-59, (January 1966).)]*

illustrates the effect of a pyrohydrolysis step on the removal of uranium from the thorium–uranium oxide. After 2.5 hr the residual uranium concentration in the bed was approximately 1000 ppm, and a subsequent 2-hr fluorination period resulted in essentially no further uranium volatilization. At this point (designated *P* in Fig. III-1) the bed was fluidized with a mixture of 80 vol.% steam in nitrogen at 500°C for 2 hr. This pyrohydrolysis step converted the ThF_4 to ThO_2 of high surface area, and uranium was thereby freed for subsequent recovery by reaction with fluorine. The fluorination step was resumed, and, after 2.5 hr of fluorination, a second pyrohydrolysis step was performed. After an additional hour of fluorination, the uranium concentration in the bed was reduced to 100 ppm, which was equivalent to 99.5% uranium volatilization from the bed material.

Workers at ORNL[2,5] are studying the oxidation of HTGR fuel as a head-end step for the recovery of uranium by aqueous methods. Oxidation tests were performed in a 4-in.-diameter fluid-bed reactor. (A description of this equipment appeared in a previous issue of *Reactor Fuel Processing*.[6]) In a typical test, chopped or crushed HTGR fuel was added to 20 kg of alumina, and the bed was heated to the ignition temperature of 650°C. The oxygen flow rate was 1.3 scfm. The temperatures of the center of the bed and the reactor wall were maintained at 750 and 700°C, respectively. In general, oxygen utilization was 95%, and the off-gas composition was 90 vol.% CO_2, 5 vol.% CO, and 5 vol.% oxygen. Oxidation rates up to 1.4 kg of carbon per hour were achieved in continuous pilot-scale tests.

Laboratory-scale tests[5] were performed to determine the distribution of fission products after oxidation of HTGR fuel for 6 hr. At 800°C, approximately 35% of the cesium and 96% of the ruthenium were volatilized. At 700°C, 1.1% of the cesium and 65% of the ruthenium were volatilized. In each case, practically all the fission products were trapped in the cool end of the combustion tube, and nearly all remaining activity was removed from the off-gas by filtration with sintered metal filters. In tests in which the carbide fuel was burned in a gas deficient in oxygen, only a small amount of cesium and ruthenium was volatilized at 800°C.

PRETREATMENT OF CARBIDE FUELS FOR VOLATILITY PROCESSING

Several methods for treating graphite- or carbon-base fuel materials in preparation for uranium recovery by volatility techniques are being studied at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium.[7,8] These methods involve the conversion of uranium carbide to a uranium oxide (UO_3, U_3O_8, or UO_2) or to uranium tetrafluoride. Nitric acid vapors[7] are used at temperatures between 320 and 400°C to transform uranium carbide to epsilon UO_3. The carbon content of epsilon UO_3 prepared at 400°C is approximately 4 wt.% of the original carbon present in the UC. The concentration of carbon in the product can be reduced to 2 wt.% of the original carbon when the nitric acid vapor oxidation is conducted at 450°C.

Other oxidizing agents that have been evaluated include air, carbon dioxide, and steam.[7] A temperature of 650°C is required to initiate the reaction between uranium carbide and carbon dioxide, whereas oxidation of UC with steam commences at 500°C. Oxidation of UC with CO_2 or steam leads to the formation of UO_2.

In the processing of sintered uranium carbide fuel materials, it is desirable to convert the carbide to a powdered material prior to fluorination. A series of tests was made at CEN[9] to evaluate the use of oxygen, air, and water vapor as agents for converting sintered UC bodies to a powdered oxide. The tests were performed in a fluid-bed reactor, 5.6 cm in diameter, which contained 60 to 400 g of UC sintered pellets and 400 g of alumina. It was observed that the use of air and oxygen–nitrogen mixtures at temperatures between 300 and 800°C was not effective in producing a powdered-oxide material. In fact, in most tests, the UC was only partially converted to oxide; evidently the formation of an oxide layer on the surface of the carbide limits further chemical attack on the pellet. Water vapor (100% H_2O) was a much more effective agent than water–oxygen mixtures or oxygen–nitrogen mixtures in producing a powdered-oxide material. The maximum yield of powdered oxide (81%) was obtained in 2 hr with the use of 100% H_2O at 500°C. When water vapor is diluted with nitrogen, the conversion of UC to oxide decreases markedly.

Uranium monocarbide will react with hydrogen fluoride gas to form uranium tetrafluoride and, depending on the reaction temperature, either free carbon or paraffinic hydrocarbons:

$$UC + 4HF \rightarrow UF_4 + C + 2H_2 \quad (1)$$

$$UC + 4HF \rightarrow UF_4 + \frac{C_nH_{2n+2}}{n} + \frac{(n-1)}{n} H_2 \quad (2)$$

At high temperatures (>200°C) the hydrofluorination of UC proceeds primarily according to reaction 1 with the production of small amounts of volatile CH_4, C_2H_6, C_3H_8, and C_4H_{10}. Above 350°C the last three materials appear only in trace quantities. At lower temperatures (between 50 and 200°C) long-chain saturated waxes are produced (reaction 2), and the reaction rate is limited by the diffusion of HF through the paraffin. An activation energy of about 4 kcal/mole has been calculated for the low-temperature reaction. The quantity of long-chain paraffins appearing in the product increases with a decrease in temperature. At higher temperatures, the paraffin evaporates and the reaction rate increases rapidly. An approximate value of 27 kcal/mole was calculated for the activation energy of the high-temperature reaction.[8]

Chloride-Volatility Processing of UO_2 Fuel

Gens[10] at ORNL is investigating, on a laboratory scale, a method for reprocessing UO_2 fuels based on reaction of the oxide fuel with carbon tetrachloride and chlorine to form volatile chlorides of uranium and plutonium. Since the rate of chlorination of sintered UO_2 and UO_2-PuO_2 fuel pellets with CCl_4-Cl_2 mixtures is too low to be of practical interest, the oxide fuel material is first converted to U_3O_8 or $U_3O_8-PuO_2$ by reaction with oxygen at 500 to 800°C. The product is a material of high specific surface which exhibits a high reactivity toward chlorinating agents. Oxidation tests[2] showed that UO_2-PuO_2 fuel pellets could be converted to $U_3O_8-PuO_2$ powder provided the PuO_2 content of the pellets was less than 1 wt.%. Pellets containing 20 wt.% or more PuO_2 were unaffected by oxygen even after long reaction periods at temperatures up to 800°C.

In preliminary tests[10] on the conversion of U_3O_8 powder to volatile UCl_5 and UCl_6, it was observed that the use of 15 vol.% CCl_4 in an inert gas at 400 to 550°C resulted in the formation of large amounts of nonvolatile UCl_4 and UO_2Cl_2. When chlorine was substituted for the inert gas, no UCl_4 was found at 400 to 550°C. The mechanism for the chlorination of U_3O_8 appears to involve the formation of UO_2Cl_2 as an intermediate compound that is subsequently chlorinated to UCl_5 and UCl_6.

Pure U_3O_8 is readily converted to volatile uranium chlorides at 400 to 500°C with 85 vol.% Cl_2–15 vol.% CCl_4. With U_3O_8 containing 1 wt.% PuO_2, nearly complete volatilization of the uranium was achieved in 3 to 4 hr, but only up to 50% of the plutonium[2] was volatilized (Table III-1). Complete volatilization of plutonium was only achieved at 600°C with an excess of chlorine.

Gens has proposed[11] that the recovery of uranium may be effected by the reduction of the volatile UCl_5 and UCl_6 by carbon monoxide to produce solid UCl_4. Thermodynamic calculations have shown[11] that solid UCl_4 can be produced in high yields by a single-stage reduction of UCl_5 and UCl_6 with excess CO at 200°C.

Fluoride-Volatility Processing of UO_2 Fuel

Workers at CEN[9,12–14] are developing a fluorination process for the recovery of uranium

Table III-1 REACTION OF $U_3O_8-PuO_2$ POWDERS WITH 85 VOL.% Cl_2–15 VOL.% CCl_4 AT VARIOUS TEMPERATURES

Experiment No.	PuO_2 content of mixture, %	Temperature, °C	Reaction time, hr	Amount volatilized, %		Moles of Cl_2 used per gram-atom of Pu volatilized
				U	Pu	
1	0	400	5.5	100		
2	0	500	3.5	100		
3	1	300	5.0	14	5	3×10^6
4	1	350	2.75	35	2	6×10^5
5	1	400	4.0	99	23	8×10^4
6	1	500	3.0	93	49	1×10^4
7	1	600	3.0	59	29	3×10^5
8	1	600	6.0	100	100	7×10^4

and plutonium from UO_2 fuel based on the selective fluorination of uranium from the fuel as volatile UF_6 by the use of chlorine trifluoride. In this process the oxide fuel is treated according to the scheme

$$(U,Pu)O_2 \xrightarrow[450 \text{ to } 575°C]{O_2} U_3O_8-PuO_2$$

$$\xrightarrow[450°C]{HF} PuF_4 + UF_4 + UO_2F_2$$

$$\xrightarrow[110°C]{ClF_3} UF_6 \text{ (gas)} + PuF_4 \text{ (solid)}$$

$$\xrightarrow[500 \text{ to } 600°C]{F_2} PuF_6 \text{ (gas)}$$

An advantage of this process concept is that a nearly complete separation of uranium from plutonium is achieved in the selective fluorination step. As development work continues, it may be found that the processing steps for the pretreatment of the oxide fuel prior to the selective fluorination of uranium by ClF_3 are not required. An alternative processing scheme also under development involves the simultaneous fluorination of both uranium and plutonium to form a mixture of UF_6 and PuF_6. In this scheme the oxide fuel is first reacted with hydrogen fluoride prior to fluorination in order to minimize fluorine requirements. All reactions in the process

$$(U,Pu)O_2 \xrightarrow[450 \text{ to } 575°C]{O_2} U_3O_8-PuO_2 \xrightarrow[450°C]{HF} PuF_4$$

$$+ UF_4 + UO_2F_2 \xrightarrow[500 \text{ to } 600°C]{F_2} (PuF_6-UF_6) \text{ gas}$$

were studied in fluid-bed equipment. Of major concern in this process is establishing methods for the separation of uranium from plutonium and for the recovery of plutonium. One method under development involves the absorption of the UF_6-PuF_6 mixture in a bath of molten salts. Under the influence of oxygen-containing substances, the fluorides are transformed into a soluble uranyl halide and insoluble PuO_2. Further details on this technique are discussed later in Sec. III.

As mentioned in a previous issue of *Reactor Fuel Processing*,[15] a pilot-scale alpha–gamma facility is being constructed at CEN to study the remote chemical processing of spent-ceramic-fuel materials by fluidization techniques. Details of the construction of this facility are reported in recent quarterly reports.[9,12–14] In a paper presented at the "Symposium on Design and Construction Problems of Pilot Plants for Recycling Irradiated Fuels," Schmets, Heremans, and Pierini[16] discussed the design philosophy of the facility being constructed at CEN.

PRETREATMENT OF UO_2 FUEL FOR VOLATILITY PROCESSING

Both of the fluorination processes described above involve initial steps in which the UO_2 fuel is converted to uranium tetrafluoride by reaction with hydrogen fluoride prior to fluorination to UF_6. The sintered oxide fuel is activated for hydrofluorination by oxidation with air to U_3O_8. A series of tests has been performed[9] to evaluate the reactivity of UO_2-PuO_2 mixtures toward oxidation to $U_3O_8-PuO_2$ at temperatures between 375 and 475°C. It was observed that the extent of conversion of UO_2 to U_3O_8 was unaffected by the presence of up to 10 mole % PuO_2 in the oxide. For oxide containing 20, 25, and 30 mole % PuO_2, only 60 mole % of the UO_2 was converted to U_3O_8. Slightly greater conversion was achieved with oxide containing 60 mole % UO_2–40 mole % PuO_2. This behavior was generally independent of temperature within the range 375 to 475°C.

Hydrofluorination of U_3O_8 to form UF_4 and UO_2F_2 is carried out at 450°C by the use of 50 vol.% HF in nitrogen. In tests performed[12] with U_3O_8 derived from UO_2 containing a small quan-

tity of fission-product oxides (2 wt.%), it was observed that in the presence of fission products the time to completely react U_3O_8 with HF at 450°C was longer than for pure U_3O_8. To assure complete conversion of U_3O_8 to fluorides, it appears necessary to carry out the hydrofluorination at 500°C. Volatilization of uranium as UF_6 from the mixture containing UF_4, UO_2F_2, and fission products by reaction with fluorine at 450 to 520°C appeared to be unaffected by the presence of the fission products.

A series of experiments was performed[14] to demonstrate the conversion of sintered UO_2 containing 2 wt.% synthetic fission products to UF_6 by the reaction sequence $UO_2 \rightarrow U_3O_8 \rightarrow UO_2F_2 + UF_4 \rightarrow UF_6$. The tests were carried out in fluid-bed equipment with 4 kg of UO_2 and 2 or 4 kg of alumina as the inert bed material. Owing to the presence of fission products in the UO_2, a temperature of 500°C was required during oxidation to achieve complete conversion of the sintered oxide to powder. Subsequent reactions were, in general, unaffected by the presence of fission products.

FLUORINATION WITH CHLORINE TRIFLUORIDE

Of major concern in the development of the fluoride-volatility process for low-enriched UO_2 fuel is the establishment of methods for the separation of uranium from plutonium and for the recovery of plutonium. A method for effecting the separation of uranium from plutonium involves the selective fluorination of uranium from the mixed fluorides (UF_4–UO_2F_2–PuF_4) with chlorine trifluoride.[9,12–14] Plutonium is recovered as PuF_6 in a subsequent step by fluorination of the solid PuF_4 with fluorine. The results of laboratory-scale tests indicated[13] that the reaction of (UF_4 + UO_2F_2) with ClF_3 proceeds readily at 105°C. The rate of reaction of the mixed fluoride is less than for UF_4 alone. The presence of up to 20 mole % plutonium in the mixed fluorides does not markedly affect the rate of uranium fluorination by ClF_3. With plutonium concentrations greater than 20 mole %, the reaction rate diminishes greatly. The presence of up to 47 wt.% inert alumina in (UF_4 + UO_2F_2) does not significantly influence[12] the rate of reaction with ClF_3.

In an effort to simplify the process scheme, a series of tests was made at CEN[9,14] to evaluate the direct fluorination of sintered UO_2 pellets with ClF_3. The tests were carried out in a vertical tube 3.4 cm in diameter. At temperatures between 75 and 300°C, the reaction between sintered UO_2 and ClF_3 proceeds rapidly. Over the temperature range 75 to 165°C, the reaction rate was observed to be insensitive to the temperature; an apparent activation energy of less than 1 kcal/mole was calculated for the reaction in this temperature range. In tests employing 25 vol.% ClF_3 in nitrogen, it was observed that the rate of reaction passed through a minimum at a temperature between 165 and 300°C, and at 300°C the reaction rate was identical to that observed at 100°C. In tests performed with sintered UO_2 containing 2 wt.% synthetic fission products, it was observed that the rate of reaction of the UO_2 with ClF_3 was slightly less than the rate observed in the absence of fission products. Processing rates for the conversion of sintered UO_2 to UF_6 on the order of 3.8 kg UO_2/(hr)(dm^2) [35.3 kg UO_2/(hr)(sq ft)] have been achieved in a reactor 3.4 cm in diameter.

SEPARATION OF PuF_6 FROM UF_6

In the processing of low-enrichment fuels by the action of fluorine, a mixture of UF_6 and PuF_6 is produced. Separation of UF_6 from PuF_6 may be achieved by thermal decomposition of PuF_6 to PuF_4 or by selective reduction of PuF_6. Regnaut and Bourgeois[17] have compared the behavior of UF_6 and PuF_6 toward SO_2 and Freons to establish a method for separating UF_6 from PuF_6. At 80°C, UF_6 is only slightly reduced by SO_2 (see Table III-2); a maximum reduction (0.7%/hr) occurs with a molecular ratio of UF_6/SO_2 of 2. Hydrogen fluoride in concentrations up to 10 vol.% acts as an inhibitor. Plutonium hexafluoride is rapidly reduced by SO_2 at 10 to 100°C

Table III-2 REDUCTION[17] OF UF_6 BY SO_2

Partial pressure, torrs		Molecular ratio	HF addition,	Experiment time,	Amount reduced,
UF_6	SO_2	(UF_6/SO_2	%	hr	%/hr
242	508	0.47		5	0.1
196	206	0.95		4	0.49
242	183	1.32		8	0.7
450	150	3.0		3	0.76
540	120	4.5		3	0.45
600	100	6.0		3	0.19
630	90	7.0		6	0.06
650	65	10.0		15	0.04
375	375	1.0	4	5	0.12
485	220	2.2	8	3	0.19
450	150	3.0	10	0.45	1.3
650	100	6.5	8	5	0

with SO_2/PuF_6 ratios of 3 to 18. The extent of conversion varied between 98 and 99%.

Four varieties of Freons were evaluated as selective reductants for PuF_6: Freon-11 (trichlorofluoromethane, CCl_3F); Freon-12 (dichlorodifluoromethane, CCl_2F_2); Freon-13 (monochlorotrifluoromethane, $CClF_3$); and Freon-23 (trifluoromethane, CHF_3). The reactivity of Freons toward UF_6 and PuF_6 increases in the order: Freon-13, Freon-12, and Freon-11. Freon-13 is inert in the presence of UF_6 to 200°C and reacts slowly with PuF_6 (<2% in 3 hr). At 150°C less than 0.08% UF_6 is reduced by Freon-12 in 3 hr, whereas 83% of the PuF_6 is reduced in 45 min at 120°C. Freon-11 reacts readily with UF_6 and is immediately fluorinated to higher Freons by the action of PuF_6. On the basis of the results of this study, it appears that the use of Freon-12 at 150°C would be the most satisfactory method for the selective reduction of PuF_6. No tests were performed to evaluate Freon-12 with UF_6-PuF_6 mixtures.

DESIGN OF EQUIPMENT FOR FLUID-BED FLUORIDE-VOLATILITY PROCESSES

The objective of the U. S. Atomic Energy Commission's (AEC) fluoride-volatility program is to develop the technical data required for the design of an all-volatility commercial reprocessing plant for power-reactor fuels. Accelerated activity in this program has been prompted by the plan to construct a hot engineering-scale pilot plant at ORNL. This facility will be used to demonstrate the separation of plutonium and uranium from fission products in low-enrichment power-reactor fuels and the recovery of plutonium. Four AEC laboratories are responsible for providing the necessary data and information on process parameters and equipment design; these laboratories are Argonne National Laboratory (ANL), ORNL, BNL, and the Oak Ridge Gaseous Diffusion Plant (ORGDP).

Argonne has the responsibility of providing the data necessary to firmly establish the process flow sheet and the data necessary for the design of much of the equipment used in the facility. A description of the fluid-bed fluoride-volatility process under development at ANL appeared in a previous issue of *Reactor Fuel Processing*.[18]

Workers at ORNL and ORGDP are concerned with equipment design and layout and with safety procedures and accountability problems within the facility. The program at ORGDP has also included process scale-up studies with inactive fuel materials to evaluate equipment components. Details of the ORGDP studies have been published recently in a summary report.[19] The report reviews work on the following subjects: definition of engineering problems; radioactive heat generation in the fluid bed; costs for storage of radioactive solids wastes; criticality calculations; corrosion tests; and evaluation testing of gas filters, connectors, and gas compressors. A preliminary design of the primary fluid-bed reactor has been made[2] (see Fig. III-2). This reactor, constructed of 8-in.-diameter schedule-40 nickel pipe, will be used both for the decladding of Zircaloy-2-clad UO_2 fuel and for the fluorination of the fuel material.

Miller and Berry[20] have published the results of a survey of the information available on the corrosion behavior of candidate materials for use in the fluid-bed volatility process. Nickel

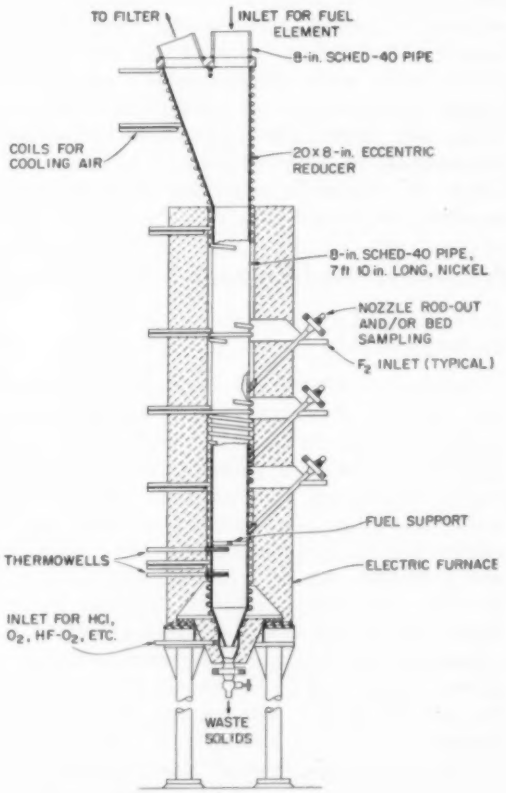


Fig. III-2 Primary reactor proposed for fluoride-volatility pilot plant.[2]

200 or Nickel 201 appear to be the optimum materials for use in the 400 to 600°C temperature range of the decladding, oxidation, and fluorination steps of the process. The survey included data for two alternative decladding techniques: decladding of Zircaloy-2 by reaction with HCl, and decladding of Zircaloy-2 and stainless steel by oxidation with gaseous mixtures of HF and oxygen. Maximum penetration rates in the HCl process, calculated from relatively short-time exposures (up to 230 hr), were less than 4 mils/month on the basis of weight change. An intergranular modification found in many specimens penetrated to an average depth of 1 mil and a maximum depth of 10 mils. The modification was somewhat greater in Nickel 201 than in Nickel 200. The possibility that the modification is deleterious has not been established. Limited data for the HF–oxygen process indicate, on the basis of weight change, that the corrosion of nickel is somewhat greater than for the HCl process. Corrosion results indicated that Duranickel Alloy 301 would probably be satisfactory as a construction material for flanges. In some instances welds made with nickel filler metal 61 corroded much more rapidly than those made with Nickel 200 or Nickel 201. Uranium hexafluoride and plutonium hexafluoride in the presence of fluorine did not appear to accelerate attack on nickel at temperatures below 500°C.

Preparation and Properties of Fluorides

FLUORINATION OF URANIUM COMPOUNDS BY BrF_5 AND BrF_3

Workers at ANL[21,22] are investigating a method for effecting the separation of uranium from plutonium based on the selective fluorination of uranium with bromine pentafluoride. Since BrF_5 converts uranium compounds to volatile UF_6 while plutonium compounds are converted to nonvolatile PuF_4, a separation between uranium and plutonium can be achieved. Plutonium can then be converted to volatile PuF_6 in a subsequent step by the use of elemental fluorine. In connection with this work, an experimental program is under way to investigate the kinetics of the reaction of BrF_5 with various uranium compounds.

A series of experiments[21] was performed in a horizontal tubular reactor to determine the kinetics of the reaction of U_3O_8 with BrF_5 over the temperature range from 250 to 400°C. The reacting gas phase contained 26 vol.% BrF_5 in nitrogen. The results showed an increase in reaction rate (volatilization of UF_6) with time at reaction temperatures of 300°C or higher. This phenomenon was attributed to the occurrence of a concomitant reaction between U_3O_8 and UF_6 producing solid UO_2F_2 and UF_4. A change in rate results when accumulation of UO_2F_2 on the surface of the U_3O_8 hinders further reaction between UF_6 and U_3O_8 and thereby allows greater volatilization of UF_6. Reaction rate constants for the initial period varied from 0.0051 min^{-1} at 250°C to 0.0266 min^{-1} at 400°C. For the second period the reaction rate constants varied from 0.0192 min^{-1} at 300°C to 0.0396 min^{-1} at 400°C.

Preliminary experiments at 300°C for the UO_3-BrF_5 and UO_2-BrF_5 reactions showed a change in the reaction rate with time similar to that observed for the $U_3O_8-BrF_5$ reaction.[21] The reaction rates for both the UO_3-BrF_5 and UO_2-BrF_5 reactions were higher than those measured for the $U_3O_8-BrF_5$ reaction.

The effects of temperature and BrF_5 partial pressure on the rates of reaction of BrF_5 with U_3O_8 and UF_4 have been determined.[22] For the UF_4-BrF_5 reaction, the temperature range was 200 to 275°C and the BrF_5 partial pressure was varied from 138 to 370 torrs. For the $U_3O_8-BrF_5$ reaction, the temperature range was 275 to 360°C and the BrF_5 partial pressure was varied from 89 to 369 torrs.

No effect of the linear velocity of the gas phase on the value of the reaction rate constant was observed for either reaction. The following equations were derived from the experimental data to represent the temperature and partial-pressure dependence of the two reactions:

For the UF_4-BrF_5 reaction,

$$\log k = 0.377 \log P - 3686/T + 4.287$$

For the $U_3O_8-BrF_5$ reaction,

$$\log k = 0.897 \log P - 1938/T - 0.4268$$

where k is the reaction rate constant, min^{-1}; T is the temperature, degrees Kelvin; and P is the partial pressure (torrs) of BrF_5. Apparent activation energies of 16.9 and 8.8 kcal/mole were calculated for the UF_4-BrF_5 and $U_3O_8-BrF_5$ reactions, respectively.

The fluorination of U_3O_8 powder by gaseous BrF_3 has been studied by Iwasaki and Sakurai.[23]

It was observed that the reaction rate increased with an increase in temperature up to 220°C, at which point the reaction decreased markedly to a minimum at temperatures between 225 and 230°C. At temperatures above 230°C the reaction rate again increased with an increase in temperature. An activation energy of 0.9 kcal/mole was calculated for the $U_3O_8-BrF_3$ reaction over the temperature range 67 to 220°C.

SORPTION OF URANIUM HEXAFLUORIDE

Decontamination of UF_6 produced by fluoride-volatility techniques can be accomplished by an absorption–desorption cycle in a bed of NaF pellets. The parameters affecting the rate of sorption and the total capacity of NaF pellets when used for UF_6 collection have been studied by workers at ORNL to provide design information for sorption beds.[2,24] A series of tests was performed to evaluate the effectiveness of two varieties of NaF pellets in terms of bed capacity and efficiency for removing UF_6 from a gas stream. The two types of pellets were (1) commercially available NaF pellets and (2) pellets fabricated from powdered NaF. Workers fabricated pellets of a high degree of structural stability from powdered NaF by blending the powder with water followed by drying at 250 to 350°C and sintering the pellets at 650 to 700°C. The two types of pellets were evaluated in a series of three sorption–desorption tests. The performance of each variety of pellet was satisfactory, and at the end of the tests neither pellet type exhibited any sign of degradation.

Smiley, Brater, and Pashley[19] at ORGDP have evaluated the use of NaF as a sorbent for UF_6 in prototype systems. A series of tests was performed in a 4-in.-diameter vertical trap containing a 7-ft-deep bed of pellets to study the effects of pellet characteristics and operating conditions on UF_6 sorption. The gas streams contained 10 vol.% UF_6, 15 vol.% F_2, and from 0 to 60 vol.% ClF_3, and the remainder was nitrogen. Operation was carried out with a sorption temperature of 120°C, a gas retention time of 80 sec, and a desorption temperature of 400°C. It was observed that the sorptive capability of fresh NaF pellets was approximately twice that of pellets which had been used in several sorption–desorption cycles. In one series of tests, the sorption capacity of the pellets for UF_6 was significantly less with a gas stream containing 30 or 60 vol.% ClF_3. In the absence of ClF_3, the sorption capacity was increased twofold. This phenomenon was not observed in subsequent tests with a different variety of pellets.

A series of experiments was performed[19] to investigate the factors affecting the integrity of pellets during extended sorption–desorption cycles. It was observed that, although pellets previously sintered at temperatures greater than 540°C were less severely degraded during several sorption–desorption cycles, the pellets, nevertheless, exhibited a much lower sorption capacity for UF_6 than pellets sintered at lower temperatures. The structural degradation of pellets apparently is not due to thermal cycling of the pellets from 120 to 400°C, but is a function of the amount of sodium fluoride–uranium hexafluoride complex made and then decomposed during each cycle.

It is apparent from the results of these tests that occasional replacement of trap charges will be necessary if NaF pellets are used for UF_6 sorption. The effective trap operating time will be influenced by the type of pellet used and the UF_6 loading. When there is no UF_6 sorption, as in the high-temperature (400°C) fission-product-removal trap, no pellet deterioration problems are expected.

Pilot-plant studies are being made at ORGDP[19] of a continuous system (Fig. III-3) for the sorption of UF_6 from a process gas stream. The process gas, UF_6 diluted with nitrogen, is first passed through NaF powder in a 6-in.-diameter 30-in.-deep stirred fluid bed at 120°C. Sodium fluoride is fed continuously to the reactor, and

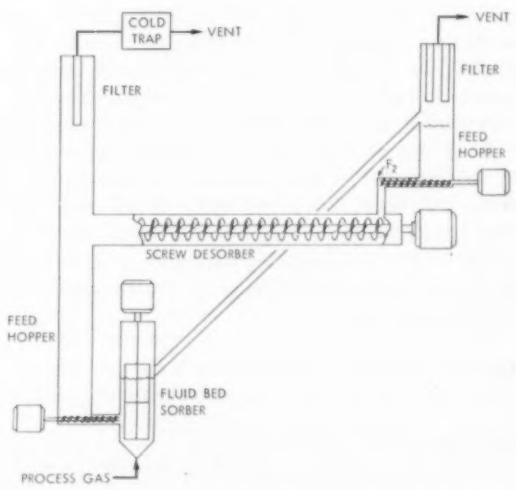


Fig. III-3 Continuous UF_6 sorption system.[19]

the overflow powder is transported by the outlet gases to a filter mounted above the feed hopper for a ribbon-flight screw desorber. The UF_6-loaded powder is fed from this hopper to the 6-in.-diameter 8-ft-long screw, where it is heated to 400°C to desorb the UF_6. A small flow of fluorine is maintained through the screw to prevent formation of lower valent uranium fluorides. The rotational speed of the screw is 1 to 2 rpm. The regenerated sodium fluoride collects in the fluid-bed hopper. The total NaF inventory in the system is 200 lb.

Performance tests have been made with NaF of particle size 100% through 20 mesh and particle size 5% through 325 mesh. The fluid bed has been operated with gas velocities of 0.15 to 0.7 ft/sec and UF_6 concentrations of 1 to 4 vol.%. No operational problems have been noted with stirrer speeds as low as 20 rpm. Average UF_6 concentration in the off-gas has been consistently below 50 ppm. Essentially complete desorption of UF_6 has been accomplished in the screw reactor at 400°C. Screw outlet gases containing as high as 40 vol.% UF_6 have been obtained.

Complex Compound with UF_6

Malm, Selig, and Siegel[25] have prepared $NaUF_7$ and Na_2UF_8 by the reaction of UF_6 with powdered NaF dispersed in an inert solvent, C_7F_{16}. The reaction between UF_6 and NaF is strongly temperature dependent. In the presence of excess UF_6, the reaction goes to completion at 100°C to form $NaUF_7$. The dissociation pressure of $NaUF_7$ is about 35 torrs at 100°C. When $NaUF_7$ is heated in vacuum, UF_6 is given off rapidly and Na_2UF_8 is formed. At 300°C the decomposition proceeds further to give NaF and UF_6. Analogous compounds have been prepared from UF_6 and KF.

In recent work at ORNL,[2] complex compounds of the type $MF_6 \cdot NaF$ were prepared with UF_6, WF_6, and MoF_6 when the $MF_6 \cdot 2NaF$ complex was treated with the appropriate metal fluoride at 75°C. The temperature dependence of the dissociation pressures of the $MF_6 \cdot NaF$ compounds was found to be:

$$\log P_{mm} = 11.06 - (3.48 \times 10^3)/T \quad \text{for } UF_6 \text{ over } UF_6 \cdot NaF$$

$$\log P_{mm} = 7.44 - (2.13 \times 10^3)/T \quad \text{for } WF_6 \text{ over } WF_6 \cdot NaF$$

$$\log P_{mm} = 7.29 - (1.83 \times 10^3)/T \quad \text{for } MoF_6 \text{ over } MoF_6 \cdot NaF$$

where P_{mm} is pressure in millimeters of mercury and T is the temperature in degrees Kelvin.

VAPOR–LIQUID EQUILIBRIA FOR UF_6–BrF_5 AND UF_6–NbF_5

Vapor–liquid equilibria in the BrF_5–UF_6 system have been reported by Liimatainen and Swanson.[26] Isotherms were obtained at 70 and 90°C. The system showed positive deviation from ideality with no azeotrope. At 3 atm total pressure, the relative volatility of the BrF_5–UF_6 binary varied from 1.80 to 1.09 over the complete range of compositions.

An investigation is under way at ORNL[2] to determine the vapor–liquid equilibria of UF_6–NbF_5 in the pressure region 0 to 12 atm at 80 to 250°C. Isothermal data have been obtained at 150°C. The data were fitted with the Scatchard–Hamer equations:[27]

$$\log \gamma_1 = A + 2z_1 [(V_1 B/V_2) - A] z_2^2$$

$$\log \gamma_2 = B + 2z_2 [(V_2 A/V_1) - B] z_1^2$$

where γ_i = activity coefficient of i

$z_1 = x_1/[x_1 + (V_2/V_1)\, x_2]$

$z_2 = x_2/[x_2 + (V_1/V_2)\, x_1]$

V_i = molar volume of i

x_i = mole fraction of i

A, B = constants, which were varied to produce the best fit of the data, assuming that $P = \gamma_1 x_1 P_1^0 + \gamma_2 x_2 P_2^0$, where P is total pressure and P_i^0 is vapor pressure of i at 150°C

With uranium hexafluoride as component 1, the values of A and B that produced the best fit were: $A = 0.6$; $B = 0.75$.

The critical constants of NbF_5 are being measured. Preliminary data[2] indicate the critical temperature to be between 480 and 520°C and the critical pressure to be between 40 and 50 atm.

PREPARATION AND PROPERTIES OF FLUORIDES

Preparation of Fluorides. Pure anhydrous cerium tetrafluoride has been prepared by Asker and Wylie[28] by the reaction between CeO_2 and fluorine at 350 to 500°C. The fluorine dissociation pressure of CeF_4 at 500°C was measured to be less than 0.5 mm. At higher temperatures CeF_4 sublimes incongruently, and at 835 to

841°C, CeF_4 melts with extensive decomposition producing a fluorine-poor liquid and a fluorine-rich vapor. Cerium tetrafluoride is readily reduced to CeF_3 at low temperatures (400°C) by ammonia and water vapor. At 1000°C, CeF_4 is completely converted to CeO_2 by water vapor.

A tentative phase diagram for the system CeF_4-CeF_3 has been proposed by Asker and Wylie.[29] There is no solid solution in the terminal phases, and the system is essentially eutectic in character.

A method for purifying ZrF_4 by sublimation techniques has been described by Yeatts and Rainey.[30] A single-stage vacuum sublimation step at 700 to 800°C was sufficient to reduce the concentration of iron from 550 to less than 100 ppm. Pretreatment of the impure ZrF_4 with NH_4HF_2 and the use of an elaborate baffling system in the sublimation equipment gave a product material containing 250 ppm oxygen.

In a study of the properties of NbF_5, Schäfer and associates[31] prepared NbF_5 by the reaction of K_2NbF_7 with AlF_3. Niobium pentafluoride is reduced to NbF_4 by the reaction with niobium metal at 350°C. The tetrafluoride disproportionates under suitable conditions to produce $NbF_{2.5}$ and NbF_5. At temperatures greater than 700°C, $NbF_{2.5}$ is prepared by the reaction of NbF_5 with niobium metal. A preliminary study of the NbF_5-TaF_5 system indicates that the binary forms a complete solid solution exhibiting nearly ideal behavior. In other work, Edwards[32] has determined the structures of NbF_5 and TaF_5 by X-ray single-crystal techniques. The unit cell has a tetrameric structure with metal atoms at the corners of a square linked by linear bridging fluorine atoms. The two compounds are isostructural with MoF_5.

Thermodynamic Properties. A program is under way at ANL to determine thermodynamic properties of substances of interest in the fields of high temperature and atomic energy by the use of fluorine-bomb calorimetry. Recent work has concerned the measurement of the enthalpies of formation of ruthenium pentafluoride,[33] yttrium trifluoride,[34] and arsenic pentafluoride[35] by combustion of the elements in fluorine. The standard enthalpies of formation, $\Delta Hf^\circ_{298.15}$, of crystalline RuF_5 and YF_3 were -213.4 ± 0.3 and -410.7 ± 0.8 kcal/mole, respectively. The derived thermal data for the formation of AsF_5 (gas) at 25°C are:

$$As(c,\text{black}) + {}^5/_2F_2(\text{gas}) \rightarrow AsF_5(\text{gas})$$

Energy of formation ($\Delta Ef^\circ = \Delta Ec^\circ$), kcal/mole	-294.70 ± 0.19
Enthalpy of formation ΔHf°, kcal/mole	-295.59 ± 0.19
Entropy of formation ΔSf°, cal/(deg)(mole)	-51.53
Gibbs energy of formation ΔGf°, kcal/mole	-280.23 ± 0.19

The vapor pressure of liquid thallous fluoride, TlF, has been measured[36] over the temperature range 420 to 820°C, and the results were correlated by the equation $\log P_{mm} = 7.841 - 5450/T \pm 0.016$, where T is the temperature in degrees Kelvin. Mass-spectrometric observation of the vapor showed that the dimer was the preponderant species and that trimer and tetramer existed in very small proportions. Calculations based on vapor-pressure data indicated that the dimer would constitute 63 vol.% of the vapor at the melting point of TlF (595.4°K) and 59 vol.% at the normal boiling point (1099°K). The enthalpies of evaporation at 1000°K were 23.7 kcal/mole to form the monomer and 22.5 kcal/mole to form the dimer.

The enthalpy of formation of solid TlF was determined relative to that of TlI by the measurement of (1) the enthalpy of solution of TlF in water and subsequently (2) the enthalpy of precipitation of TlI from the same solution.[37] The average value for the enthalpy of formation of solid TlF, ΔHf°_{298}, was –77.8 kcal/mole.

Molten-Salt Fluoride-Volatility Processing of Aluminum-Base Fuel Alloys

By W. J. Mecham

At ORNL the molten-salt fluoride-volatility process developed earlier for zirconium-base fuels[38] has been adapted to the processing of aluminum-base fuels.[2,39] These types of fuel alloys are the major ones employed in reactors fueled with highly enriched uranium. The processes for the two fuel types are essentially the same; the flow sheet for aluminum-base fuels that is employed in pilot-plant studies is shown in Fig. III-4. The basic flow sheet was reviewed previously for the zirconium-base fuel.[40]

This flow sheet encompasses the dissolution of fuel elements in a molten fluoride salt

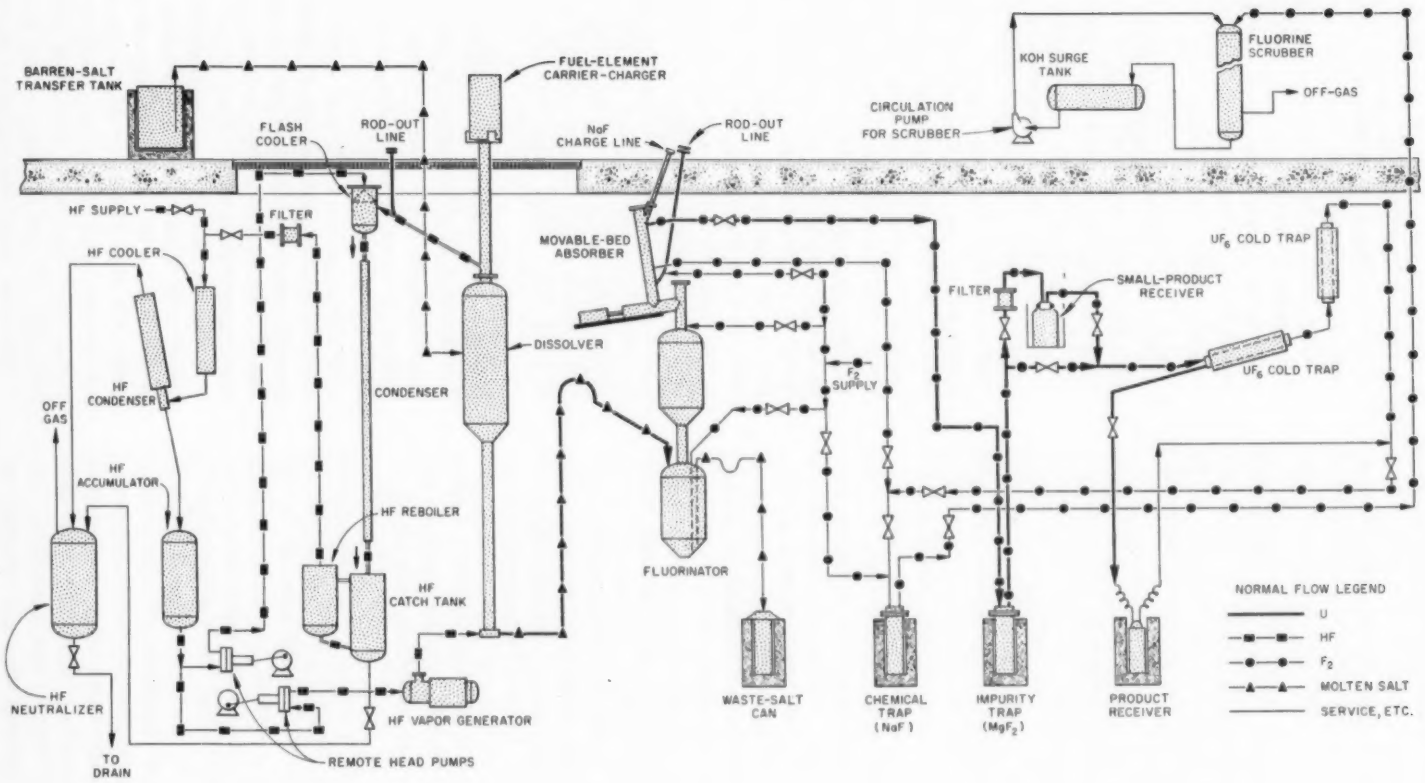


Fig. III-4 Process flow diagram of volatility pilot plant.[2]

sparged with HF, fluorination to separate the uranium (as UF_6) from the salt and from most of the fission products, and further purification and recovery of the UF_6. These steps are described below for the aluminum-base fuel.

FUEL AND SALT CHARGING

Aluminum–uranium alloy fuel elements were lowered into the dissolver and then covered with a molten fluoride salt at about 600°C. The composition of the $KF-ZrF_4-AlF_3$ salt was such that the desired amount of aluminum could be dissolved without the production of a melt with a liquidus temperature exceeding 550°C.

FUEL DISSOLUTION

The metallic fuel plates were dissolved when anhydrous HF was sparged through the melt at about 600°C, and the metal was thereby converted to AlF_3 and UF_4. Time for complete dissolution ranged from 11 to 20 hr. After dissolution the salt was transferred to the fluorinator for uranium removal.

URANIUM FLUORINATION

Salt was held in the fluorinator at about 550°C. Sparging of the salt with fluorine for about $1\frac{1}{2}$ hr converted the UF_4 to UF_6. The volatile UF_6 leaving the fluorinator entered the movable-bed absorber; most of the fission products remained in the fluorinator salt.

PRODUCT PURIFICATION AND RECOVERY

The UF_6 leaving the fluorinator was further purified in a sorption–desorption cycle. Most of this purification was done in the movable-bed absorber, which was filled with NaF pellets. The pellets in the first section (at 400°C) retained some of the fission products and corrosion products but allowed the UF_6 to pass through. Pellets from this section of the absorber were intermittently discharged into the fluorinator, and the sorbed contaminants were thereby returned to the waste salt. In the next section of the movable-bed absorber (at 150°C), the NaF sorbed the UF_6 but allowed some of the remaining contaminants to flow out into the off-gas system. After fluorination and sorption were completed, the entire movable-bed absorber was heated to 400°C. The UF_6 was desorbed, passed through a bed of MgF_2 pellets for removal of technetium and neptunium, and condensed as a solid in cold traps.

The contaminants discharged to the off-gas system were passed through a caustic fluorine scrubber and a trap designed to remove TeF_6, a constituent of major activity. The trap consisted of nickel mesh heated to 400°C, a gas cooler, and an activated-charcoal bed at ambient temperatures (less than 50°C). Although appreciable amounts of tellurium were trapped, a significant fraction was carried through to the off-gas stack. Some of the tellurium was released after evolution from the fluorinator had ceased; thus the trap extended the release time of tellurium to the atmosphere.

PILOT-PLANT RUNS WITH IRRADIATED FUEL

After several runs with simulated fuel elements, four pilot-plant runs were made with aluminum–uranium alloy fuel having ^{235}U burnups of 24 to 31% to study uranium decontamination from fission products. The fuel cooling times in the four runs were as follows: $1\frac{1}{2}$ years, 175 days, 80 days, and 25 days.

The nonrecoverable uranium losses were less than 1% in each of the runs. Decontamination factors for the hexafluoride product were those shown in Table III-3. These decontamination factors, although considered satisfactorily high for all elements except molybdenum and antimony, were about a factor of 10 less than those in the equivalent zirconium-processing runs. The lower decontamination factors in the fourth (short-cooled) run were believed to result from possible nonoptimum conditions of operation of the dissolver and/or the movable-bed absorber.

Cationic contamination of the UF_6 product was higher than desirable, and analyses were too inconsistent for valid interpretation. Impurity levels of 0.1 to 1% in the product were obtained for molybdenum, aluminum, and sodium. The presence of molybdenum indicated incomplete separation in the moving-bed absorber; the presence of sodium, presumably as the nonvolatile NaF, suggests a filter failure. No explanation was made for the aluminum impurity.

Phase diagrams of the salt mixtures and corrosion data are presented in the reports. In general, corrosion behavior for the aluminum process was similar[2,39] to that previously reported for the zirconium process[41] with respect to the high-nickel alloys of interest as construction materials.

Table III-3 OVERALL DECONTAMINATION FACTORS* IN VOLATILITY PILOT-PLANT RUNS WITH IRRADIATED ALUMINUM–URANIUM ALLOY FUEL[2]

Run No.	Decay time, days	Nonvolatile isotopes					Volatile isotopes					
		Sr†	^{91}Y	^{137}Cs	^{140}Ba	^{144}Ce	^{95}Zr	^{95}Nb	^{99}Mo	Ru‡	Sb§	Te¶	^{131}I
RA-1	~570	6×10^9		$>4 \times 10^9$			$>2 \times 10^8$	$>9 \times 10^8$		1×10^6	8×10^6		
RA-2	175	5×10^8		2×10^9		$>4 \times 10^{10}$	$>3 \times 10^9$	$>2 \times 10^9$		6×10^6	$>1 \times 10^7$		
RA-3	80	$>4 \times 10^9$	4×10^9	$>1 \times 10^8$	$>2 \times 10^8$	$>6 \times 10^9$	$>4 \times 10^9$	$>7 \times 10^9$		2×10^8	1×10^6	7×10^7	$>2 \times 10^6$
RA-4	25	5×10^6	1×10^7	2×10^5	$>9 \times 10^7$	1×10^7	5×10^7	1×10^7	36	$>6 \times 10^6$	1×10^3	6×10^5	4×10^6

*Decontamination factor is defined as the ratio of the quantity of nuclide in the fuel per gram of uranium to the quantity in the product per gram of uranium.
†^{89}Sr and ^{90}Sr.
‡^{103}Ru and ^{106}Ru.
§^{125}Sb and ^{127}Sb.
¶^{127m}Te, ^{129m}Te, and ^{132m}Te.

Removal of UF_6 and PuF_6 from Molten Salts

For the extension of molten-salt fluoride-volatility techniques to power-reactor fuels, satisfactory recovery of both uranium and plutonium is required. In this section results of recent experiments at ORNL for the molten-salt fluoride-volatility technique are described.[2] However, the plans at ORNL are to place more emphasis on development of fluid-bed techniques as an alternative to molten-salt techniques for the fluoride-volatility processing of power-reactor fuels. Accordingly, experimental work on some of the molten-salt techniques is being brought to a close.

VOLATILIZATION OF PuF_6 FROM MOLTEN SALTS CONTAINING HIGH CONCENTRATIONS OF URANIUM

One of the key operations in the application of the molten-salt fluoride-volatility process is the recovery of plutonium as the hexafluoride. However, PuF_6 is not easily volatilized from the molten fluoride by direct fluorination. Previous work showed that more than 99% of the PuF_6 could be volatilized from molten fluoride salts in 20 to 30 hr. Subsequently an experimental study was made of a scheme to improve the plutonium fluorination rate by the use of a high uranium concentration in the melt to act as a fluorine carrier. In five runs with initial uranium concentrations in the $LiF-NaF-ZrF_4$ melt of up to about 25%, the percentage of PuF_6 volatilized in 1 hr was about 32%, compared with about 15% volatilized in 1 hr in an earlier test with no uranium present. Initial plutonium concentrations were in the range of 805 to 1140 ppm. These results were considered to be unsatisfactory. No further work is planned.

RECOVERY OF PLUTONIUM AND URANIUM FROM FALLING MOLTEN-SALT DROPLETS AND FROM BEDS OF SOLID PARTICLES BY FLUORINATION

A laboratory investigation of the fluorination of UF_4 and PuF_3 from falling droplets of molten $NaF-ZrF_4$ salt was made to determine the chemical feasibility of recovery of uranium and plutonium in a falling-drop tower.[2] In this process the falling droplets are contacted with fluorine to convert the plutonium and uranium in the salt to hexafluorides. The potential advantage of this approach is that the rate of corrosion of the process container may be less than for a fluorinator operated batchwise with a continuous salt phase and fluorine sparging.

Data on uranium volatilization from falling droplets of molten salt have been extended from the work reported previously[38] to include five additional salt blends. Results indicate that this approach to recovery of the uranium can lead to much faster removal than that provided when fluorine is bubbled through a pool of the molten fluorides.

With respect to the volatilization of plutonium by fluorination of falling droplets of fluoride melts, five laboratory experiments were made. Plutonium removals of 21 to 87% were achieved for drop diameters of 53 to 177μ at temperatures of 500 to 640°C in a 4.5-ft tower. From the results it was concluded that a spray-fluorination process for plutonium recovery is chemically feasible.[2]

Correlations were presented in the report for the data on uranium and plutonium removal rates: The fraction of uranium removed was proportional to the initial concentration, but the fraction of plutonium removed was independent of the initial concentration. Only minor further chemical work is planned. No engineering evaluation was presented.[2]

The possible recovery of uranium from fluoride salt by fluorination of solid salt particles was also investigated in the laboratory. In comparison with bubbling fluorine through molten fluoride, this method also would be much less corrosive to the container. In five laboratory-scale fluorinations, it was found that the salt sintered at the operating temperature. The prospects for this method were considered unfavorable. Work on this technique has been terminated.[2]

Chemistry of Molten Lithium Fluoride–Beryllium Fluoride

Molten mixtures of LiF and BeF_2 have been under study as a carrier solvent for enriched UF_4 in fluid-fueled nuclear reactors. The oxide chemistry of this system is of interest because oxide is a principal impurity to be dealt with in preparative work and because metal oxides are known to be only sparingly soluble in $LiF-BeF_2$ mixtures. The limited solubility of uranium oxides or other oxides is of concern because precipitates would interfere with stable reactor operation.[42]

A study has been made in which the transpiration method was used to equilibrate dilute gaseous mixtures of HF and H_2O in hydrogen carrier gas with molten $LiF-BeF_2$ mixtures varying in composition from 0.25 to 0.80 mole fraction BeF_2, both saturated and unsaturated with crystalline BeO, in the temperature range 500 to 700°C. The primary data from the measurements were used to obtain the equilibrium quotient for the reaction of HF and H_2O with solid BeO and dissolved BeF_2. Equilibrium quotients were also obtained for the formation of oxide and hydroxide ions in the liquid phase.[42]

These equilibrium quotients were employed to determine: (1) thermodynamic activities of LiF and BeF_2 in the mixtures, (2) thermodynamics of liquid BeF_2, (3) stability of hydroxide in the melt, and (4) solubility of BeO in the $LiF-BeF_2$ system as a function of temperature.[42]

Compact Pyrochemical Processes

By L. Burris and G. A. Bennett

Compact pyrochemical processes are nonaqueous processes for the recovery and purification of partially burned reactor fuels. They possess utility for the recovery of ceramic fuels (such as oxides or carbides) as well as metallic fuels. Although processes are available for handling fuels directly,[43] i.e., without dissolution in any solvent media, most of the pyrochemical processes make extensive use of molten-metal and -salt systems as processing media. The metal-solvent systems consist principally of various alloys, usually binary alloys, of zinc, cadmium, magnesium, and copper. The salt systems are halide (generally chloride) salts of alkali and alkaline-earth metals.

These processes possess features which should be economically beneficial, particularly in fast reactor fuel cycles. These features include (1) the ability to accommodate short-cooled high-burnup fuels of both ceramic and metallic types with consequent reduction in fuel inventory, (2) the use of small process volumes, which makes the processes suitable for use in a small plant, (3) a decrease in criticality problems because of the absence of aqueous solutions, (4) the direct production of concentrated fission-product wastes, and (5) the recovery of expensive alloying agents. Since these processes effect only partial decontamination, all handling operations must be performed remotely.

Processes for Future Fast Reactor Fuels

SALT-TRANSPORT PROCESSES

A significant recent development in the pyrochemical processing of future reactor fuels is the continued successful demonstration of the salt-transport concept[44] by the Chemical Engineering Division of ANL. Salt-transport processes are those in which the fissile and fertile constituents of the fuel are selectively and incrementally transferred from one liquid-metal solvent to another when a molten-salt phase is cycled between the two metal solvents. The selective transport of the valuable fuel constituents takes place as a result of differences in distribution coefficients and solubilities of the fuel constituents in the two metal/salt solvent systems. Because only small volumes of metal and salt solutions are required and because separation factors are high, the process is easily adapted for use in small, compact plants.

To date most of the experimental work at Argonne has been carried out with the copper–

magnesium and zinc–magnesium alloy systems as the liquid-metal solvents. This work[45,46] has indicated that uranium–plutonium–fission-product separations can be effected at 800°C when uranium and plutonium are selectively transferred (in sequence, if desired) from a liquid copper–magnesium alloy to a zinc–magnesium alloy by means of halide salts containing a high percentage of $MgCl_2$. Simultaneously, magnesium is transferred to the copper–magnesium phase. This alloy system[46] offers the advantages of a reasonably good single-stage separation of rare earths from plutonium, good uranium and plutonium transfer rates, and internal control of the magnesium concentration in the copper–magnesium alloys by the dissolution of excess solid copper in the system as magnesium is transferred into the copper–magnesium alloy.

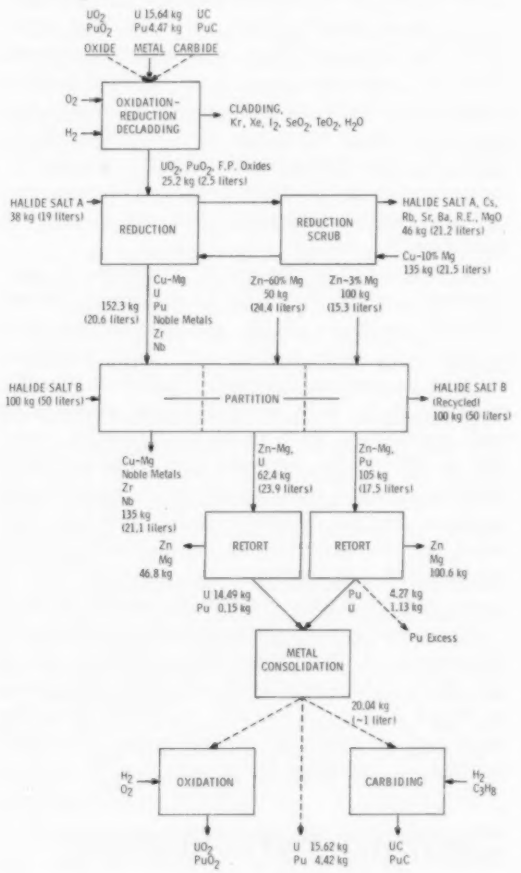
Cadmium-based systems[45] are being considered as alternatives to copper–magnesium systems because they offer the advantages of lower operating temperatures (~600°C), a possibility of the use of steel vessels, and the absence of nonvolatile solvent metals that cannot be removed by a retorting step. These systems have the disadvantage, however, that fission-product separation factors are lower, and multistage contacting is therefore required, particularly for the plutonium–rare-earth separation.[45]

The use of a cadmium–zinc–magnesium alloy[46] would also permit low-temperature operation (500 to 600°C); at low magnesium concentrations rapid uranium transfer would be achieved. However, the transfer rate is extremely sensitive to magnesium concentration, changing markedly with only a slight variation in magnesium concentration. Control of the magnesium concentration at the necessary low level would be difficult.

A conceptual salt-transport process,[47] which utilizes copper–magnesium and zinc–magnesium alloys and which would accommodate a variety of fuels, is shown in Fig. III-5.

In this conceptual flow sheet, the first step is an oxidative decladding operation in which oxide fuels are released from cladding. Carbide and metal fuels are converted to oxides in such a step. The oxides are then reduced in the presence of a halide flux phase by a copper–10% magnesium alloy in which the reduced elements also dissolve, or precipitate if their solubility is exceeded. The highly electropositive fission elements and the alkali, rare-earth, and alkaline-earth elements redistribute strongly to the salt phase and are removed in it. Then, by taking advantage of the widely different distribution coefficients and solubilities for uranium and plutonium in metal phases of different compositions, the uranium and plutonium are separated by selective transfer to separate metal phases.

Plutonium and uranium are next recovered from their solvent metals by a retorting step to remove volatile zinc and magnesium. After consolidation of the metal products by a melting step, the plutonium–uranium alloy is con-


UO2 PuO2
U 15.64 kg Pu 4.47 kg
UC PuC
OXIDE
METAL
CARBIDE
O2
H2
OXIDATION-REDUCTION DECLADDING
CLADDING, Kr, Xe, I2, SeO2, TeO2, H2O
UO2, PuO2, F.P. Oxides 25.2 kg (2.5 liters)
HALIDE SALT A 38 kg (19 liters)
REDUCTION
REDUCTION SCRUB
HALIDE SALT A, Cs, Rb, Sr, Ba, R.E., MgO 46 kg (21.2 liters)
Cu-10% Mg 135 kg (21.5 liters)
Cu-Mg U Pu Noble Metals Zr Nb
152.3 kg (20.6 liters)
Zn-60% Mg 50 kg (24.4 liters)
Zn-3% Mg 100 kg (15.3 liters)
HALIDE SALT B 100 kg (50 liters)
PARTITION
HALIDE SALT B (Recycled) 100 kg (50 liters)
Cu-Mg Noble Metals Zr Nb 135 kg (21.1 liters)
Zn-Mg, U 62.4 kg (23.9 liters)
Zn-Mg, Pu 105 kg (17.5 liters)
RETORT
RETORT
Zn Mg 46.8 kg
Zn Mg 100.6 kg
U 14.49 kg Pu 0.15 kg
Pu 4.27 kg U 1.13 kg
Pu Excess
METAL CONSOLIDATION
20.04 kg (~1 liter)
H2 O2
OXIDATION
CARBIDING
H2 C3H8
UO2 PuO2
U 15.62 kg Pu 4.42 kg
UC PuC

NOTE: Quantities shown represent daily processing rate for 1000-MWe(e) reactor core after 10% burnup and with 20% plutonium in core at discharge. This flow sheet can also be used for blanket material.

Fig. III-5 Conceptual pyrochemical process for oxide-, metal-, or carbide-fuel fast breeder reactor core.[47]

verted to oxides or carbides or left as metal, as desired. The plutonium–uranium product could subsequently be fabricated to fuel elements and recycled to the reactor core or blanket. The flow sheet shown would provide uranium and plutonium recoveries of 99% or better.

The driving force in a salt-transport process depends on the difference in concentration of the transferring element in the salt above the two solvent alloys. The concentration of the transferring element in the salt is the product of its solubility in the salt times its distribution coefficient.* Some information on these quantities for systems of interest have been obtained. Laboratory data have shown that the distribution coefficient of uranium between molten $MgCl_2$ and copper–magnesium alloys at 800°C decreases from 0.27 at 9 wt.% magnesium to a minimum value of about 0.12 at 16 wt.% magnesium and then increases to an extrapolated value of about 0.50 for 100% magnesium.[48] Data[45] of this type have been correlated and are presented in Fig. III-6, which presents the maximum uranium and plutonium concentrations possible in 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl salt above uranium- or plutonium-saturated alloys of specified composition at 600°C. It is evident from these data that high concentrations of uranium (>1 wt.%), and resultant high uranium transfer rates, can be achieved in the equilibrated salts by using the solvents cadmium–magnesium or cadmium–zinc–magnesium at very low magnesium concentrations.

The solubility of plutonium in zinc–magnesium alloys is of interest since, with the copper–magnesium/molten salt/zinc–magnesium system, uranium is collected in a zinc–80 wt.% magnesium alloy, and plutonium in a zinc–2 to 3 wt.% magnesium alloy. The solubilities of plutonium in these alloys are as follows:[49]

Alloy	Pu solubility, wt.%		
	600°C	700°C	800°C
Zn–2 wt.% Mg	0.33	2.33	7.8
Zn–3 wt.% Mg	0.28	2.22	8.0
Zn–80 wt.% Mg	50.1	49.8	51.8

*Distribution coefficient (k_d)

$$= \frac{\text{wt.\% of transferring element in flux}}{\text{wt.\% of transferring element in metal}}$$

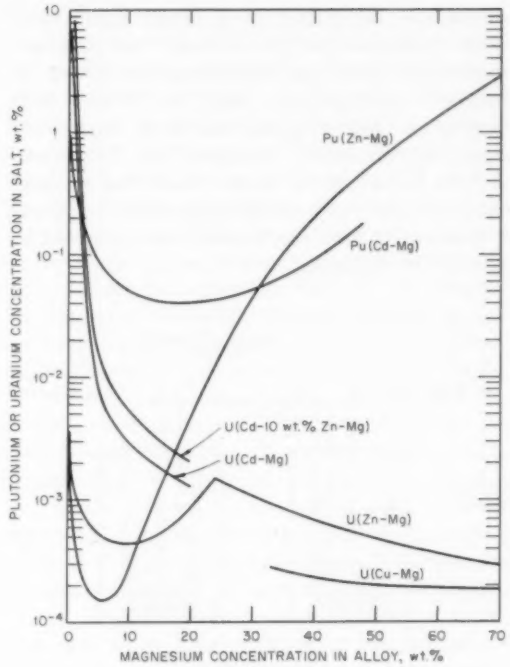


Fig. III-6 Plutonium or uranium concentration[45] in 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl salt above saturated alloy at 600°C.

Engineering Demonstration Run

The system copper–magnesium/molten-salt/zinc–magnesium was used in an engineering demonstration[45,47] run at 800°C. The reduction and salt-transport steps shown in Fig. III-5 (but with solutions of slightly different compositions) were used to recover uranium from a $6\frac{1}{2}$-kg unirradiated charge consisting of a mixture of oxides of uranium (5 kg) and of several key fission products (cerium, zirconium, molybdenum, and ruthenium).

In the reduction step, uranium, zirconium, and nobler metal oxides in a 30 mole % $MgCl_2$–30 mole % NaCl–40 mole % KCl salt were reduced by copper–8 wt.% magnesium. Most of the uranium metal, as it was formed, precipitated in the copper–8 wt.% magnesium alloy. The bulk of cerium remained in the halide salt. This salt, containing cerium and MgO reaction product, was removed and discarded as waste.

In the salt-transport step, uranium from the molten copper–8 wt.% magnesium alloy was transferred incrementally to a molten mag-

nesium–35 wt.% zinc alloy when $MgCl_2$ was cycled between the two alloys. This was accomplished with the molten-metal alloys in adjacent vessels (see Fig. III-7) and with charges of molten $MgCl_2$ that were alternately pressured through a transfer line from one alloy to the other. In each vessel the salt and metal phases were mixed to promote chemical equilibration; then the phases were allowed to separate by settling.

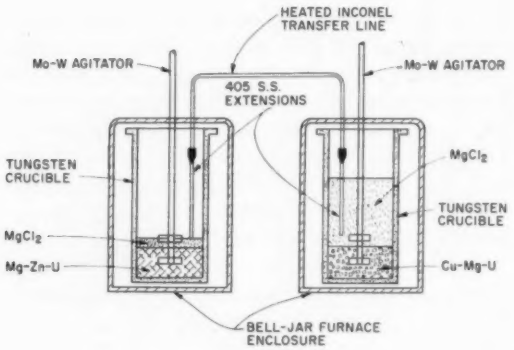


Fig. III-7 Schematic of salt-transport equipment.[47]

The net uranium transfer achieved after 14 cycles was about 88% of the 5 kg charged, which was in excellent agreement with theoretical predictions. At this point the run was terminated. Had the transfer continued in accord with theory, a 99% uranium recovery would have been achieved after about 22 transfer cycles. The rate of uranium transport tails off as the source solvent becomes highly depleted in uranium. A very satisfactory zirconium removal of 97.5% was achieved.

Materials Evaluation

A supporting program is under way at ANL to find inexpensive, easily fabricated materials for these salt-transport processes. In corrosion tests of steel and iron,[46] Croloy 16-1, a readily fabricated ferritic stainless steel similar to type 405 stainless steel, corroded at a fairly high rate in a copper–10 wt.% magnesium–2 wt.% uranium alloy and in a magnesium–35 wt.% zinc–1 wt.% uranium alloy at 800°C (~2 mils/24 hr for both alloys in the presence of a 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl salt). Consequently this material could only be used in applications where contact with the metal/salt solvent system is for a limited time, such as transfer lines. On the other hand, cast-iron crucibles exhibited no detectable corrosion or deterioration on exposure to the copper–10 wt.% magnesium–2 wt.% uranium/salt system for 170 hr at 800°C or to a cadmium–8 wt.% zinc–4 wt.% uranium/salt system for 290 hr at 600°C. More extensive tests of cast iron are therefore planned.

Tungsten is the most satisfactory material for containment of high-zinc alloys. A previous test[48,50] of an agitator blade, fabricated of pressed and sintered tungsten containing 0.1 wt.% nickel to reduce porosity of the finished tungsten shape, resulted in no evidence of deterioration on exposure to zinc/47.5 mole % $MgCl_2$–47.5 mole % $CaCl_2$–5 mole % MgF_2 at 800°C for 200 hr. Testing[46] of this material was extended by exposure of additional coupons, as agitator blades, which were used to stir a zinc/50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl system for 380 hr at 800°C. No appreciable corrosion or structural changes were observed. It is concluded that a small nickel addition to the tungsten does not significantly affect the corrosion properties in zinc/salt systems and that tungsten with 0.1 wt.% nickel would be acceptable for process requirements.

"Vitreous" carbon, a product of Société le Carbone of France, possibly could be used as a crucible liner in that it has properties similar to glass, being microscopically sealed and impervious to gas, but fragile. The corrosion resistance of this material to zinc–magnesium–uranium/halide-salt systems and copper–magnesium–uranium/halide-salt systems is being determined.[45,47–49] An analysis of all runs completed to date indicates that this material is resistant to both systems (containing up to 10 wt.% uranium) at 800°C and therefore has excellent potential as a container material for these systems.

CONTINUOUS EXTRACTION

Engineering work related to the development of continuous molten-metal–molten-salt extraction processes is also under way at Argonne. Initial experiments[49] were designed to permit examination of metal–salt extraction kinetics for transient reactions in packed col-

umns. A 1.4-in.-ID extraction column, which has a 36-in. packed section, is now being used to determine the mass transfer of rare-earth elements between countercurrent metal and salt phases under steady-state conditions. Such a countercurrent extraction experiment was performed to study the transfer of cerium from a molten cadmium phase (cadmium–10 wt.% zinc–5 wt.% magnesium–1 wt.% cerium) to a molten-chloride-salt phase (50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl), and 88% of the cerium was transferred (material balance: 92%). The height equivalent to a transfer stage was about 15 in., which is in excellent agreement with the earlier transient tests. This result is encouraging with respect to the feasibility of metal–salt countercurrent extraction processes.

SALT-CYCLE PROCESS

Further developments on the salt-cycle process[51] for processsing mixed uranium dioxide–plutonium dioxide fuels have been reported by the Pacific Northwest Laboratory (formerly Hanford). In this process a mixture of powdered U_3O_8, PuO_2, and fission-product oxides which has been separated from cladding is dissolved in molten chloride salt, and separation of uranium, plutonium, and fission products is effected by electrolytic and chemical precipitation methods. Essentially complete (99.7%) recovery of plutonium from a salt-cycle melt could be achieved by a two-step precipitation process. The LiCl–KCl melt was first sparged with an O_2–Cl_2 stream at 575°C, thereby precipitating 95% of the plutonium as PuO_2. The melt was then sparged with a H_2–argon stream, which precipitated the balance of the plutonium along with a small fraction of the uranium. Neodymium-147 and uranium decontamination factors as high as 110 and 700, respectively, were obtained. Spectrophotometric studies were reported which indicated that precipitation of PuO_2 during the O_2–Cl_2 sparge was a slow process, requiring about 5 hr for equilibrium to be obtained at 575°C.

The operation of the Salt-Cycle Process in the High Level Radiochemistry Facility was terminated after 1.5 years of essentially continuous operation.[52] Preceding shutdown, a codeposition, two bath cleanup electrolyses, and a decladding test on a vibratory-compacted PRTR (Plutonium Recycle Test Reactor) fuel rod were carried out. The codeposition produced 12 lb of 2 wt.% PuO_2–UO_2 with an oxygen-to-uranium ratio of 2.02. Appreciable success was obtained in controlling the back electromotive-force readings of the cell (a strong function of the plutonium-to-uranium ratio of the deposit at the melt interface) by controlling the O_2/Cl_2 ratio of the sparge gas. The first of the bath cleanup depositions consisted of sparging the melt with 100% oxygen and electrolyzing until the melt was depleted. Analysis revealed that 99% of the uranium and 81% of the plutonium were removed. The second cleanup deposition was a high potential electrolysis on a molybdenum cathode to remove fission products. A vibratory-compacted fuel rod that had received an exposure of 4000 Mwd/ton in the PRTR was declad quite readily in less than 5 min with waste losses of 0.2 to 0.3%. Approximately 30% of oxide adhering to the cladding was located near the end cap, probably because of insufficient vibration at that point.

Benedict et al.[53] have discussed the current status of the salt-cycle process. Their paper summarized the development of remote operations to produce fuel for recycle to the reactor. In the recycle scheme, remote operations are required since short-cooled irradiated fuel is processed. Decladding, codeposition of mixed oxides, and fuel refabrication were performed in remote equipment. Iodine behavior and plutonium precipitation were studied in the laboratory, and chlorine recovery was demonstrated in the cold pilot plant.

Research and development work on the Salt-Cycle Process was terminated in 1965 as a part of a reduction of effort in preparation for the completion of the Plutonium Recycle Program. Final reports are being prepared.[53a]

CONVERSION OF FLUORIDES TO OXIDES IN MOLTEN-SALT MEDIA

In a previous issue of *Reactor Fuel Processing*,[54] it was reported that investigators at Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium, are studying the conversion of uranium and plutonium fluorides to the oxides by means of reactions in molten-chloride media. This procedure is being developed for the purpose of reconverting the products of fluoride-volatility processes to oxides for recycle to oxide-fueled reactors (see the beginning of this section of *Reactor Fuel Processing* for a discussion of the fluoride-volatility processes).

In this process, fluorides of uranium or plutonium (UF_4, UF_6, PuF_4, PuF_6) are dissolved in a molten-chloride-salt mixture, such as the LiCl–KCl eutectic. Sparging of the salt with an oxygen-containing gas (such as an oxygen–HCl mixture) permits plutonium to be precipitated from the solution as PuO_2 and uranium to remain in the solution as uranyl ion. The uranium can be recovered in a later step either by electrodeposition of UO_2 on a graphite cathode or by chemical precipitation of UO_2 by hydrogen sparging. The results of the latest work on the processing of uranium fluorides are contained in a series of quarterly reports.[55–58]

One of the investigations discussed in these reports was carried out to obtain information on the mechanism of the reaction of UF_6 upon dissolution in molten salts.[56] It was found that the ratio of U^{4+} to U^{6+} in the salt bath, after dissolution, remained relatively constant at about 4 to 1, regardless of whether the LiCl–KCl eutectic bath had been dried or not or whether the drying agent was HCl or chlorine. In the three experiments reported, the amount of UF_6 dissolved varied between 60 and 82% of the amount charged, with the greater dissolution occurring in the undried bath.

In another series of experiments, care was taken to dehydrate the LiCl–KCl bath more completely before electrolysis as a method of improving the purity of the UO_2 product by reducing the alkali and halide contaminants.[56,57] In one such experiment a quantity of about 30 g of UF_6 was introduced into a bath of 300 g of LiCl–KCl eutectic. After oxidation of the bath by a mixture of HCl and oxygen, the bath was dried by a current of pure HCl that had been passed over $AlCl_3$. The HCl-injection period was 6½ hr, at a flow rate of 55 liters/hr. Under these conditions the dew point of the $HCl–H_2O$ (HF) mixture leaving the bath was lowered to −55°C, instead of −20°C as reached in previous tests.

The results obtained are as follows:

Oxygen-to-uranium ratio	2.002
Form of crystals	cubic
Attachment of UO_2 on graphite electrode	Very good
Impurities, ppm	
Li^+	11
Na^+	180
K^+	25
F^-	90
Cl^-	50
Total impurities, ppm	356

In three previous tests the total impurity contents were 817, 579, and 756 ppm.

The influence of the composition of the bath was studied.[57] Previous investigations had shown that very pure UO_2 can be produced from UF_6 when the LiCl–KCl eutectic bath contains only a small proportion of fluorides. When the concentration of fluorides increases, as it does when UF_6 is introduced into the bath, the melting point of the salt increases from 354°C (the eutectic melting point) to about 750°C when about half of the chlorine has been replaced by fluorine and then decreases to about 550°C when all of the chlorine has been replaced by fluorine. Because lower temperatures than these are required with Pyrex, the bath must be regenerated. Too-frequent discard of the baths, which would still contain substantial amounts of uranium and/or plutonium, would increase product losses.

One proposed regeneration method[57] attempted was transforming the fluorinated bath into a chlorinated bath by bubbling gaseous HCl through the bath. However, this approach is not practical since the equilibrium constant of the reaction

$$LiF + HCl \rightleftharpoons LiCl + HF$$

is not favorable, and only KF is capable of being transformed into KCl. Also, the phase diagram indicates that when all the lithium is in the form of LiF and all the potassium is in the form of KCl, the melting point of the bath exceeds 750°C, with accompanying corrosion problems.

A possible solution to this problem is the use of the ternary salt, 16 mole % LiF–40 mole % NaCl–44 mole % KCl, as the bath.[57] The melting point of this bath does not exceed about 650°C, when the bath is either partially or entirely constituted of fluorides. Two electrolysis experiments were carried out with the ternary salt at 640°C. Crystals of UO_2 that adhered well to the cathode were formed, but microscopic examination revealed the UO_2 to be covered with white spots, which are probably insoluble fluorides. These conditions of temperature and composition constitute the limits for the use of Pyrex as the container material for the electrolysis reaction.

The limits on Pyrex and the need to decrease the irregularity of the electrolytic deposit of UO_2 on the cathode led to a test of a graphite container for carrying out the conversion.[58]

This was unsatisfactory because the time necessary to oxidize the UF_4 to UO_2F_2 is noticeably lengthened by the reducing action of the graphite walls and because the graphite is attacked by both the fluorinated compounds and oxygen. A larger Pyrex[58] container (500-g LiCl–KCl capacity instead of 300 g as used previously), which allowed the use of two graphite anodes located at each end of a central graphite cathode in order to obtain a more uniform deposit on the graphite, was tested. Although very good attachment of UO_2 to the anodes and excellent UO_2 yield (86%) were obtained, a comparatively long electrolysis time (24 hr) was required to achieve these results.

DRY PROCESSES

Although laboratory work on pyrochemical processing at Atomics International has been concluded,[59] summary reports are still being distributed on the processes investigated. One such report, by Bodine, Guon, and Sullivan,[43] discusses second-cycle AIROX reprocessing and pellet refabricating of highly irradiated uranium oxide. As discussed in the previous issue of *Reactor Fuel Processing*,[60] the AIROX process involves oxidizing refractory UO_2 fuel in air or oxygen and then reducing the resultant U_3O_8 powder in hydrogen. A finely divided UO_2 powder is obtained after several oxidation–reduction cycles. Conventional techniques, performed remotely, can then be used to fabricate refractory UO_2 shapes and to assemble fuel clusters for further irradiation.

The objective of the work described in the Bodine[43] report was completion of the final link in the AIROX processing; namely, to show that highly irradiated–reprocessed fuel can be reirradiated and reprocessed through an additional reactor fuel cycle. This was done by AIROX-processing UO_2 that had been irradiated to burnups from 5700 to 21,000 Mwd per metric ton of uranium, reirradiating the refabricated pellets for an additional 10,000 Mwd per metric ton of uranium, and AIROX-reprocessing and -refabricating the second-cycle irradiated UO_2 into pellets. In the second processing–fabrication cycle, these pellets behaved similarly to unirradiated UO_2 during decladding by oxidation, particle-size reduction by oxidation–reduction, and pellet refabrication by cold pressing and sintering. Also, mixtures of UO_2 and stable isotopes of fission products simulating burnups of 100,000 Mwd per metric ton of uranium were irradiated to 5000 Mwd per metric ton of uranium and AIROX processed. Results indicated that fuel of this level of burnup can be reprocessed by AIROX.

Processes for Current Reactor Fuels

EBR-II SKULL-RECLAMATION PROCESS

The skull-reclamation process is being developed at Argonne specifically for the recovery of the 5 to 10% of uranium charge that is left in the melt-refining crucible as oxidized skull after melt refining of partially spent fuel from the EBR-II reactor. The chemistry and technology developed for this process will also be applicable to the processing of a variety of other uranium-bearing fuels, such as oxides, carbides, and metals.

The details of this process, which was recently simplified, were reported in previous issues of *Reactor Fuel Processing*.[60,61] The revised process was demonstrated in pilot-plant runs[62] and is currently being tested at Argonne in plant-scale equipment (~4.25 kg of uranium per batch) for later installation in the EBR-II Fuel Cycle Facility at Idaho. The plant-scale equipment consists of:[45] (1) a reduction furnace for carrying out reduction of the skull oxide and partial purification of the uranium in a large (14 in. in outside diameter by 26 in. high) tungsten crucible and (2) a retorting furnace for evaporating magnesium and zinc metals away from the uranium-product solution and thereby isolating the uranium metal for return to the main fuel stream.

In all, 10 plant-scale skull-reclamation runs have now been completed.[49] Mechanical operations, namely, charging of materials, heating, mixing, sampling, and transferring molten metals and fluxes from the furnace to exterior receivers, have been performed without difficulty.

Conditions were demonstrated under which satisfactory uranium recovery and purification were achieved. Cerium removal was satisfactory in all runs; however, inadequate removals of molybdenum and ruthenium were obtained. More vigorous agitation, higher temperature, and longer reaction time will be provided in the next series of runs to improve the removals of molybdenum and ruthenium. Moreover, fluoride-free flux will be used in the noble-metal extraction step since results of preliminary experiments indicated that fluoride-free flux

provided increased extraction of molybdenum, ruthenium, and zirconium. Since a fluoride-free flux tends to increase uranium losses in the reduction step of the process, fluoride (as CaF_2 or NaF) will be added to the flux after the noble-metal extraction step. After this series of modified tests is completed, the equipment will be adapted for remote operation in the EBR-II Fuel Cycle Facility at Idaho.

Following the present series of runs, the reduction furnace was disassembled for examination.[48] The condition of all components ranged from good to excellent. No corrosion of the furnace top or body was observed. Condensed zinc, magnesium, and flux were found on the internal heat shields, but this had not interfered with furnace operations.

The final step in the skull-reclamation process consists of retorting, or solvent evaporation, to recover the uranium from the uranium product solution. In this step[49] the magnesium–zinc–uranium ingot is first transferred to a large beryllia crucible ($8\frac{1}{2}$ in. in outside diameter by 17 in. in overall height by 0.5 in. in wall thickness) in the retorting furnace; then the magnesium–zinc is distilled under vacuum at 650 to 750°C from the uranium-product solution; finally the uranium is melted (~1200°C) to form an ingot. Four plant-scale retorting runs[49] (~30 kg of charge material) were completed with the use of zinc–magnesium–uranium ingots that were products of previous skull-oxide reclamation runs. Operation of the equipment was satisfactory. Although an isostatically pressed beryllia crucible showed hairline cracks after two runs, a thixotropically cast beryllia crucible was in good condition after similar usage.

FUSED-SALT ELECTROLYSIS

A paper on the purification of uranium by fused-salt electrolysis has been published by Mukaibo, Kanno, and Kokubo[62] of Tokyo University. In their experiments, synthetic spent fuel composed of uranium alloys containing zirconium and molybdenum to simulate fission products was used for the anode. Molten zinc was chosen for the cathode, because of its adaptability to continuous operation. The electrolytic refining was carried out in a NaCl–KCl–UF_4 fused-salt system at 750°C and in a KCl–LiCl–UCl_3 system at 500 to 600°C.

In the case of the NaCl–KCl–UF_4 system, at 750°C and with cathodic current densities of 190 to 400 ma/cm^2, the cathodic current efficiencies obtained were 20 to 60%, with a bath voltage in the range 1 to 3 volts. Continuous operation, however, was disturbed by dendritic deposits on the cathode container.

In the case of the KCl–LiCl–UCl_3 system, the UCl_3 concentration was 10 wt.% at 500°C, the cathodic current density was 100 to 250 ma/cm^2, bath voltage was 1.2 to 2.5 volts, and the cathodic current efficiencies were 40 to 90%. The electrolysis in this case could be maintained for an appreciable period. The uranium was recovered by vacuum distillation of the uranium–zinc alloy obtained on the cathode. The decontamination factors were determined to be 10 to 40 for zirconium and 30 for molybdenum.

Metal Purification and Preparation Processes

PURIFICATION OF METALS BY VARIOUS MELTING TECHNIQUES

Spriet[63] has presented results of the purification of plutonium by horizontal zone melting and by "electrodiffusion," i.e., solid-state diffusion of point defects in metals under the influence of an electric field. The effects of these treatments were monitored by spectrographic analysis, chemical analysis, and metallography. In zone melting, most of the impurities present in substantial concentration in plutonium are transported at zone velocities of about 8 mm/hr. In electrodiffusion the substitutional impurities (in practice, metallic impurities) move toward the anode, whereas interstitials move toward the cathode; the higher the temperature, the more pronounced is the phenomenon, irrespective of the phase concerned.

PREPARATION OF METALS BY REDUCTION OF THEIR COMPOUNDS

The work of Thompson[64] on the reduction of plutonium dioxide may have applicability to future reactor fuels. Attempts to reduce PuO_2 with calcium or barium to form a coalesced mass of plutonium metal were unsuccessful. Molten fluoride fluxes to dissolve CaO or BaO were not effective in promoting the reaction, nor was mechanical agitation. The major difficulty was the rapid separation of the reactant phases. Observable yields (~70%) of coalesced plutonium metal were obtained only when a

$CaCl_2-CaF_2$ flux was used and when aluminum metal was the reductant.

A previous issue of *Reactor Fuel Processing*,[65] reported the successful demonstration of continuous electrowinning of plutonium metal from plutonium trichloride at Hanford. A recent report by Soine[66] reported the completed work on process scale-up. This work established the conditions necessary for a cell capable of electrowinning plutonium metal from plutonium trichloride. The cell was operated once at 600 g/hr for short periods of time with a total average throughput of 410 g/hr. Several runs were made at lower throughputs. The majority of the runs were of one-shift duration, although several runs, attempted during the later stages of the work, lasted for 12 to 16 hr.

The process is capable of handling $PuCl_3$ that contains 10 to 20% unchlorinated material (oxide). The upper limit of unchlorinated material that can be tolerated without a reduction in the processing rate was not determined, but may be as high as 50%. In one small-scale run, plutonium metal was produced at a rate of about 65 g/hr and at an electrical efficiency of 65%.

The product was of good quality. Densities ranged up to 19.4, and the impurity level was about the same as that of the feed. Because of the high decomposition potential of $PuCl_3$, little or no purification was observed. In some cases the product was lower in purity than the feed material because of the introduction of corrosion products from hardware used with the cell. The tantalum cathode seemed to contribute excessive amounts of tantalum to the product. Tungsten was satisfactory as a cathode material.[52a]

No differences in cell performance could be positively attributed to cathode current density, which ranged from 0.25 to about 8 amp/cm^2. Cathode electrical efficiencies were consistently in the 60 to 80% region.

The plutonium content of the cell at the end of a run, regardless of the length of the run, consisted of about 200 g of metal and 200 g of slag ($PuCl_3$). This was solubilized fairly easily by hydrochloric acid for subsequent aqueous processing.

At the termination of this work, cell life was the essential unsolved problem. The best results pointed to extrapolated lifetimes of 10 to 15 kg of throughput (for ceramic cells). Metal cells would be capable of greater total throughputs (>100 kg), but the present development indicates a lower processing rate (about 50% of that for ceramic cells).

Miscellaneous

The practical applications of thermodynamics to plutonium-process reactions at high temperature were discussed by Leary and Mullins.[67] They pointed out that the important high-temperature reactions for processing plutonium involve equilibria between the liquid metal and a fused-salt system and that attainment of equilibrium is usually faster by many orders of magnitude in liquid phases than in solid phases. Consequently the application of appropriate thermodynamic data and estimates is of major importance in selection of the proper reaction system. The extraction of impurities, such as radionuclides, from molten plutonium into fused-salt media is an example cited of a high-temperature plutonium process for which thermodynamic considerations are of principal importance. Although in many reactions the activity coefficients are not known, it was shown that useful estimates of the concentrations at equilibria can be made if ideal solution behavior is assumed or if the activity coefficients are estimated from the phase diagrams, when available.

A U. S. patent[68] was recently granted to Erler, Peray, and Petit (assigned to Commissariat á l'Énergie Atomique) for their uranium-purification method, which was based on the work reported at the XVIIth International Congress of Pure and Applied Chemistry[69] in Montreal in August 1961. The process was briefly described in the preceding issue of *Reactor Fuel Processing*.[60]

A survey paper that discusses various methods, including pyrochemical, for the chemical treatment of irradiated fuel was presented by Faugeras.[70]

Evaluation of Remote Systems

By W. J. Mecham

The technical and economic evaluation of remote systems is an essential part of the development of low-cost commercial fuel-cycle

operations. This view was the major theme of the 1965 American Nuclear Society Conference on Remote Systems Technology. The proceedings of this conference included 33 major papers describing installations and programs planned to further this evaluation of remote systems. The papers dealt with fuel-reprocessing facilities, remote devices and techniques, hot-laboratory facilities, and special-purpose facilities.[71]

Experience with the Full-Scale Fuel Cycle Facility for the EBR-II Reactor

The EBR-II Fuel Cycle Facility, operated by Argonne at the National Reactor Testing Station in Idaho, is essentially a full-scale reprocessing and refabrication facility now serving the 60-Mw metal-fueled fast Experimental Breeder Reactor (EBR-II). The facilities consist of two hot cells: one is rectangular with an air atmosphere, and the other is annular with an argon atmosphere. Disassembly and reassembly operations are performed in the air cell, and actual fuel reprocessing and preparation of metal fuel pins are carried out in the argon cell. All fuel operations are accomplished completely remotely with powered manipulators, master-slaves, and self-powered machines. Viewing is by means of large shielding windows, and light is provided by mercury-vapor lights. The cells have now been operated for approximately two years (one year with radioactivity). Experiences with regard to cell operation reported in the article pertain to the maintenance of argon-atmosphere purity and the reliability of the remote-control devices. The dry argon atmosphere imposes unique requirements for brushes on electric motors and for electrical insulation.[71a]

In the first step of fuel reprocessing, a fuel-element-removal machine is used to apply precisely the force necessary to dismantle the incoming fuel assemblies. Another machine is employed for mechanical removal of the cladding from the fuel pin. Reprocessing is done by melt refining (a low-decontamination pyrochemical process) in compact equipment that is operated and maintained completely remotely. Approximately 18 hr of operating time is required to clean, declad, and melt-refine the fuel from one subassembly received from the EBR-II reactor. Operating experience in this part of the plant showed that the proper metals must be selected for the fabrication of mechanical components to prevent excessive wear of unlubricated metal-to-metal surfaces.[71b]

In the demonstration of fuel refabrication (injection casting and the various cladding and assembling operations), no significant difference in operating performance was obtained with respect to irradiated and unirradiated material. Punch cards were used to keep data that are to be incorporated in a program for economic evaluation. A general problem in the refabrication steps is the mechanical matching of the output of one machine to the input of the succeeding machine. A combination of automatic and manipulator operations was used. The report states that the features of compliance and feedback possessed by manipulator systems are highly useful in such transfers and feeding operations, and the advantages of these features have not as yet been supplanted by those of machines designed for automatic operations.[71c]

Bench-Scale Hot Facility for Fluoride Volatility

A miniature processing plant for irradiated fuel, employing the fluid-bed fluoride volatility process, has been operated in a hot cell at Argonne. The primary objective of this work is to obtain information regarding the separation of uranium and plutonium from fission products and the distribution of fission products within the unit. Hot operations were started in November 1964 with irradiated fuels of both the highly enriched uranium-alloy type and the low-enrichment oxide fuels.[71d]

Remote Devices and Techniques

With continuing application of remote devices and techniques to operations more closely approximating commercial production, there has been a trend away from a high degree of reliance on general-purpose remote-handling equipment to more specialized devices and techniques. However, there is a tendency for information on the specialized devices and techniques developed for specific applications to be lost and not incorporated into the general body of knowledge of remote-systems technology. This adverse tendency can be opposed by systematic reporting.[71]

Specialized developments were illustrated by papers on servo manipulators for high-energy

accelerators, a device for the remote determination of gas pressure and volume within encapsulated fuel elements, a high-temperature tensile-testing machine for irradiated structural materials, cryogenic irradiation equipment, photogrammetric techniques, remotely operated underwater devices for determining the dimensional stability of fuel elements, equipment for removal of contaminated filters, and a semiremote cutting technique for the removal of a chemonuclear loop.[71]

An application of television to remote operations is an experimental head-controlled television system to provide viewing for a manipulator operator. Some method for good visual feedback is a necessary part of a complete manipulator system. Although television suggests itself as a possibly more flexible and economical method of viewing than windows or periscopes, the quality of a television picture is poor compared to that of the optical methods. Television picture quality is a matter of image resolution which, in turn, depends on the number of scanning lines of the system. In practice it is necessary to limit the angle of view to get even fair resolution. This is so because with a smaller angle (and hence smaller field of view), greater image detail is achieved for a given number of lines of resolution of the television image. With a reduced field of view, however, movement of the television camera is required to see the full area of operations of the manipulator. The use of an appropriate servo system allows movement of the head of the operator to control the pan and tilt motions of the camera and the corresponding image on the viewing monitor. The necessity of holding the head completely rigid when the camera is to be pointed in a fixed direction is avoided by transmittal of only head motions in excess of about 10° to the camera-positioning systems.[71e]

The report of the proceedings also contains papers concerning hot-laboratory facilities and technical notes on special-purpose applications.[71]

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Section

IV

Reactor Fuel Processing

Waste Disposal

By P. Fineman

Treatment of Low- and Intermediate-Level-Activity Wastes

Ion Exchange

At Oak Ridge National Laboratory (ORNL), work is continuing on the development of the water-recycle process (Fig. IV-1) for the treatment of low-level-activity aqueous wastes (LLW).[1,2]

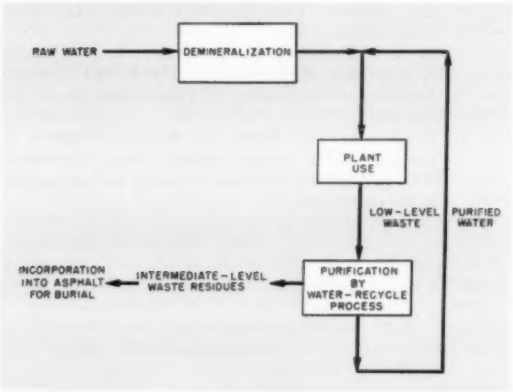

Fig. IV-1 Water-recycle process.[2]

This process is based on the following: (1) demineralization of all raw water entering a plant and (2) decontamination and demineralization of the LLW so as to recycle for reuse to the plant the purified water that is produced. The purification of the LLW is carried out by the following steps: (1) a batch clarification step using zeta-potential*-controlled additions of coagulant and coagulant aid and (2) a demineralization step to treat the supernatant from step 1. For additional removal of radioactive species such as cobalt and ruthenium, the second sorption step utilizing activated carbon may be carried out.

In recent work two laboratory tests of this process (see Fig. IV-2) were completed with the use of ORNL LLW (pH, ~ 7) to which ^{106}Ru and ^{60}Co tracers were added. In the demineralization step of the process, a mixed bed of cation and anion exchangers was used in one test and separate-bed cation and anion exchangers were used in the other test. In both tests the cation ion exchanger was Dowex 50W, and the anion exchanger was Dowex 1. The overall decontamination factors for individual nuclides (Table IV-1) ranged as follows: test 1, 20 for antimony to 6500 for cobalt; test 2, 160 for zirconium–niobium to 12,000 for cobalt. Removal of the nuclides was accomplished primarily in the clarification and ion-exchange steps. As expected, the ion-exchange step removed most of the cesium and strontium; and, because of the activated carbon, significantly more ^{60}Co was removed. Breakthrough of some nuclides occurred either simultaneously with bulk ion breakthrough or soon after, as indicated by measurement of specific conductance. Thus it appears that continuous monitoring of specific conductance could serve as a simple indicator of ion-exchange-bed exhaustion.

Demineralization capacity (0.1% specific-conductance breakthrough) with the mixed-bed ion exchanger was about 470 bed volumes, and with the separate-bed cation and anion exchangers it was about 420 bed volumes. (However, demineralization capacity is expected to be as high as 2500 bed volumes with treatment of LLW that contains only the salts added through plant use.) The two ion-exchanger systems produced water of satisfactory quality; the

*Zeta potential keeps particles in suspension and hinders or prevents their agglomeration.

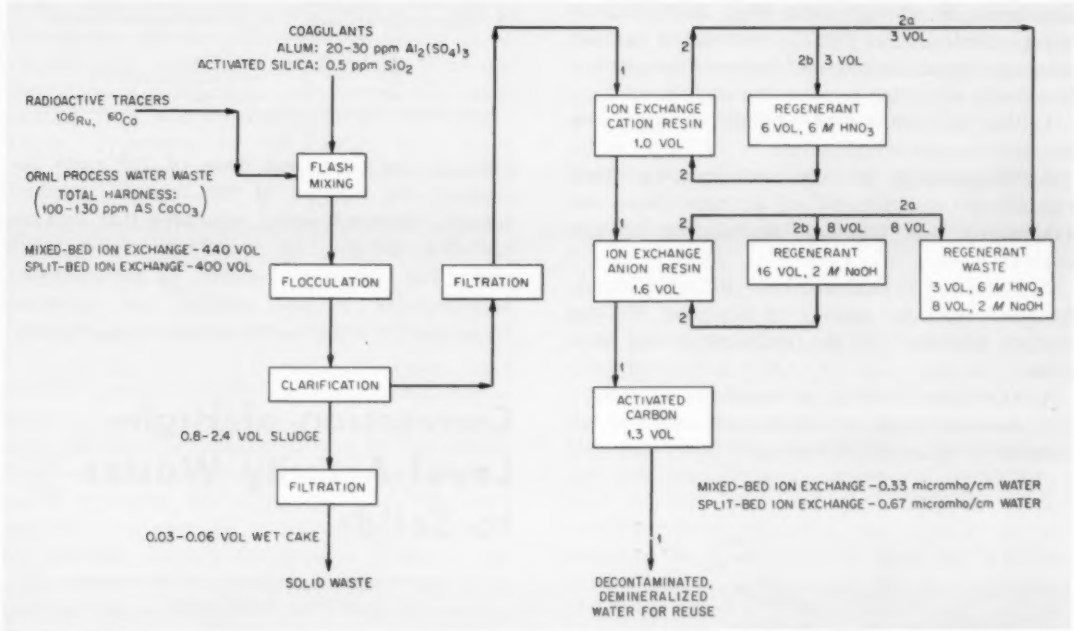
COAGULANTS
ALUM: 20–30 ppm $Al_2(SO_4)_3$
ACTIVATED SILICA: 0.5 ppm SiO_2
RADIOACTIVE TRACERS
^{106}Ru, ^{60}Co
ORNL PROCESS WATER WASTE
(TOTAL HARDNESS: 100–130 ppm AS $CaCO_3$)
MIXED-BED ION EXCHANGE – 440 VOL
SPLIT-BED ION EXCHANGE – 400 VOL
FLASH MIXING
FLOCCULATION
CLARIFICATION
0.8–2.4 VOL SLUDGE
FILTRATION
0.03–0.06 VOL WET CAKE
SOLID WASTE
FILTRATION
ION EXCHANGE CATION RESIN 1.0 VOL
REGENERANT 6 VOL, 6 M HNO_3
2a 3 VOL
2b 3 VOL
ION EXCHANGE ANION RESIN 1.6 VOL
REGENERANT 16 VOL, 2 M NaOH
2b 8 VOL
2a 8 VOL
REGENERANT WASTE 3 VOL, 6 M HNO_3 8 VOL, 2 M NaOH
ACTIVATED CARBON 1.3 VOL
MIXED-BED ION EXCHANGE – 0.33 micromho/cm WATER
SPLIT-BED ION EXCHANGE – 0.67 micromho/cm WATER
DECONTAMINATED, DEMINERALIZED WATER FOR REUSE

Fig. IV-2 Water-recycle flow sheet used in laboratory tests with ORNL low-level-activity waste.[2]

Table IV-1 DECONTAMINATION FACTORS OBTAINED IN LABORATORY TESTS OF THE WATER-RECYCLE PROCESS USING ORNL PROCESS WASTE (LLW)[2]

	Individual isotopes								Total rare earths	Gross gamma	Gross beta	Bulk ions (specific conductance)
	^{144}Ce	^{60}Co	^{137}Cs	^{131}I	^{106}Ru	^{125}Sb	^{90}Sr	$^{95}Zr-^{95}Nb$				
Raw Waste Analysis, dis/(min)(ml) or counts/(min)(ml)												
Process 1*	11.3	136	12.2	†	25.4	0.8	29.1	1.2	15.1	77	52	330‡
Process 2§	10.1	70.9	23.6	126.2	44.2	3.5	52.0	0.4	32.0	52	85	290‡
Overall Decontamination Factors												
Process 1	150	6,500	370	†	200	20¶	1,500	45¶	1,500	390	870	1,000
Process 2	340	12,000	2,600	430	200	300	6,300	160¶	11,000	130	1,200	500

*Process 1: Alum-silica clarification, mixed-bed ion exchange, coconut-shell activated carbon. Values for decontamination factors at 0.1% breakthrough as indicated by specific conductance measurements.

†Not determined.

‡The dimensions of specific conductance are micromhos per centimeter.

§Process 2: Alum-silica clarification, separate-bed ion exchange, bituminous coal activated carbon. Values for decontamination factors at 0.2% breakthrough as indicated by specific-conductance measurements.

¶These are minimum values, since the radioactivity in the waste water was reduced to the analytical limits of detection (background).

specific conductance (micromhos per centimeter) was 0.33 for the mixed-bed ion exchanger and 0.66 for the separate-bed ion exchangers. Separate beds may be desirable economically because regeneration is easier.

Studies are now under way to adapt the water-recycle process to continuous operation. Small-scale pilot-plant tests are also planned in order to obtain cost data.

Incorporation in Asphalt

Incorporation of intermediate-level-activity wastes (ILW) in asphalt appears to be a simple and inexpensive method for the disposal of this type waste.[3] These wastes that have a high salt or solids content contain modest levels of radioactivity; thus fission-product heating and radiation dose levels do not present serious

problems. In the process (Fig. IV-3) that is being developed at ORNL, emulsified asphalt incorporates these wastes.[4] Some of the attractive features of the process are as follows:

1. Use of emulsified asphalt, which flows readily at room temperature.
2. Evaporation at low temperatures. This minimizes entrainment of activity from the evaporator and thermal degradation of the asphalt.
3. Agitation at modest rates (100 to 500 rpm). At these speeds, mixing is adequate and the heated surfaces of the evaporator are kept clean.
4. Operation in batch or continuous manner.
5. Incorporation of soluble and insoluble activity with equal effectiveness.

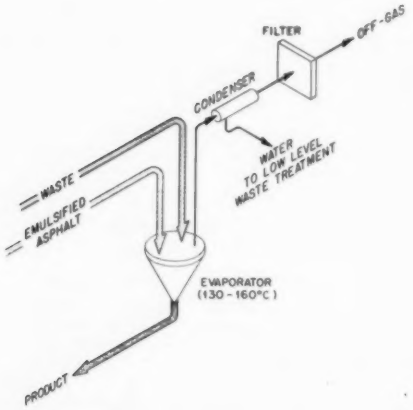

Fig. IV-3 Flow diagram of process to incorporate intermediate-level-activity waste in emulsified asphalt.[4]

Design of a pilot plant to incorporate 100-gal batches of LLW in emulsified asphalt per 8-hr shift has been completed, and installation of the pilot-plant equipment has started. Radioactive feed in the pilot-plant tests will consist of ORNL plant-level-activity waste-evaporator concentrate. As part of the program, a process hazards study has also been started.

In recent work,[4] samples of hard-based asphalt products containing 60 wt.% of ILW concentrate solids were irradiated by means of a ^{60}Co source to absorbed doses ranging from 10^6 to 10^8 rads. For doses of 10^6, 10^7, and 10^8 rads, the following effects were noted on the volume of asphalt product samples:

Absorbed dose, rads	Effect observed on sample
10^6	Negligible
10^7	Very slightly swollen
10^8	~36% increase in volume

Although an absorbed dose of 10^8 rads increased the volume of the asphalt product sample, previous work[3] indicated that this irradiation dosage had no effect on the leach rate. The long-term effect of incorporated radionuclides on the physical and chemical properties of asphalt samples is being studied.[4]

Conversion of High-Level-Activity Wastes to Solids

Engineering-Scale Equipment for Demonstration of Waste Solidification

At Pacific Northwest Laboratory (PNL), engineering-scale demonstrations of three solidification processes will be carried out with actual high-level-activity wastes in a pilot plant now being constructed.[5–9] The following processes will be tested: (1) radiant-heat spray-calcination process developed by Hanford Laboratories of Hanford Atomic Products Operation (now Pacific Northwest Laboratory), (2) pot calcination and rising-level pot-glass processes developed by ORNL, and (3) continuous phosphate-glass process developed by Brookhaven National Laboratory. The design of the prototype demonstration equipment, referred to as waste-solidification engineering prototypes (WSEP), is complete.[9] (A simplified flow diagram of the WSEP was presented in a previous Review.[10]) Procurement and fabrication of equipment items are essentially complete. The WSEP will be installed in B cell of the Chemical and Materials Laboratory (formerly the Fuels Recycle Pilot Plant). Startup of the WSEP is planned for the first half of 1966.

The WSEP is designed to process radioactive waste feed at a maximum of 10 gal/hr. This rate is equivalent to the wastes produced during the reprocessing of 1 to 3 tons of uranium reactor fuel per day. The calcines or glasses produced are collected in containers (or pots) that are 8 to 12 in. in diameter and 8 ft long. Each container is filled to a nominal level of

6 ft. Before the filled containers are sent to permanent storage, they will be placed in an intermediate storage area for long-term observation of temperature, pressure, heat-generation rate, and solidified-product characteristics. Operators of the facility have made flexibility possible by grouping associate pieces of equipment on movable modules or racks and by using auxiliary equipment (e.g., feed preparation and off-gas treatment) common to all the solidification-equipment concepts. Since all solidification processes are serviced by common off-gas equipment, only one solidification process can be operated at one time. Also, since only two positions exist for the three solidification processes, only two solidification processes may be in operating position at one time. However, the remote concept for modules or racks permits the equipment for the third solidification process to be stored until ready for testing. Design verification tests of the major items of prototype equipment are being carried out with nonradioactive feed materials. Tests of the pot calciner and its related auxiliary equipment items have been successfully completed.[6-8] Tests of the radiant-heat spray calciner are in progress.[9]

Conversion to Glasses

Effect of Composition on Phosphate-Melt Formation

In support of the WSEP, Barton at PNL is studying the formation of phosphate melts containing residues from Purex type process wastes.[11-14] In laboratory work with nonradioactive solutions, he is investigating the properties of phosphate melts corresponding to a wide range of process conditions and fuel exposure (including fuel-processing wastes containing up to 95% fission-product oxides).

In an interim report Barton[14] has summarized work with wastes containing 3, 10, and 50% fission-product oxides (the remainder of the waste is composed of process oxides). He shows that plant wastes in which fission-product oxides represent 50% of the weight of the oxides present can be successfully incorporated into a phosphate melt that is fluid at less than 900°C and thus can be transferred into a storage container. Consonant with process temperatures, two (or possibly more) optimum phosphate compositions occur near the cation (M_2O) to phosphate (P_2O_5) ratios of 2.1 and 1.0. (With ratios less than 2.6, a homogeneous system is produced.) These compositions did not produce melts having the lowest solubilities in water. However, even the melts of minimum solubility would be too soluble to allow them to be in contact with groundwater that might be used for other purposes. Therefore minimum solubility should not be the controlling factor in the decision on the composition to be used.

For a wide range of phosphate compositions, glasses were formed when the melt samples were heated to 1200°C and then quickly cooled. Glasses having a M_2O to P_2O_5 ratio of about 1 were resistant to devitrification. However, under the self-heating conditions that would exist in high-level-activity waste storage, this composition may also devitrify. In general, devitrification greatly increased the solubility of the melts produced. However, the solubility did not increase nearly so much for those melts having a minimum solubility near M_2O to P_2O_5 ratios of 2.3 and 1.0.

Work is in progress on the production of phosphate melts from simulated Purex type process wastes composed of 75% fission-product oxides and 25% process oxides.[13]

Solidification of Condensate from WSEP

Laboratory work is also under way at PNL on two methods of handling the condensate from the phosphate-glass process which is to be demonstrated in the WSEP.[15-17] The condensate is a high-level-activity waste and is composed of several acids — sulfuric and nitric acids in principal quantities and phosphoric acid in small amounts. One method[15,16] is to convert the sulfate in the condensate to a relatively insoluble melt such as lead sulfate. Mixtures of lead sulfate, sodium perborate, and lead oxide form melts below 1000°C. Experiments with a simulated condensate have been started in which the formation of lead sulfate melts is being investigated in a continuous feed melter. The other method[17] is to incorporate the condensate after neutralization into asphalt. This method appears to be suitable for this type of waste, but the high levels of radioactivity in the condensate will first have to be reduced. Ways of accomplishing this are being examined. The possibility of removing the nitric acid or the nitrates from the waste because of their detrimental effect is also being considered.

Leaching of Phosphate Glass Produced from Actual Purex-Plant Waste

In previously reported Hot-Cell Glass Experiments, phosphate glass was produced from actual plant-level-activity Purex 1WW waste.[18,19] Leaching tests with water are being performed on samples of this glass. The leach rate has remained appreciably the same [2×10^{-5} g/(cm^2)(day)] in the seven months that the tests have been conducted. These samples have also showed evidence of a minute, new phase exuding from the pores in the glassy matrix. The composition of the exudations is not known. However, since the exudations are more numerous on the surfaces corresponding to the top of the melt than on those of the bottom, it is postulated that the exudations are the result of incomplete dehydration of the phosphoric acid or of subsequent hydration of free P_2O_5 in the melt.

Hazards of Shipping High-Level-Activity Wastes Fixed in a Phosphate-Based Matrix

Because a shipping accident involving high-level-activity ceramic-fixed wastes may occur and a high-temperature fire may thereby result, a program is under way at PNL to investigate airborne fission-product release from these wastes at high temperatures.[20] Two release mechanisms are under study: volatilization and mechanical entrainment of particles in the air stream.

Currently, tests are being conducted with nonradioactive samples of phosphate-based ceramics (M/P ratio of 2.8) which simulate the composition of a waste produced in the reprocessing of a power-reactor fuel element irradiated to 20,000 Mwd/ton. The samples contained the following fission products: cesium, cerium, ruthenium, and strontium. The samples were exposed to temperatures between 1050 and 1250°C, and the following fission-product release rates were observed:[21] (1) The cesium release rate was 1 to 2%/hr. Even at temperatures of 900°C when the ceramic is not molten, releases of 0.2%/hr can be expected. (2) The release rates of cerium, ruthenium, and strontium were about 1/1000 that of cesium. This difference in release rates established volatilization as the predominant release mechanism for cesium. If entrainment had been the dominant mechanism, the release rates of the isotopes would have been nearly equal, and the volatilized particles in the experimental carrier gas would have essentially the same composition as the source material.

Fluid-Bed Calcination

Preparation and Leaching of Glass from Fluid-Bed Calcined Waste

Studies have been completed at the Idaho Chemical Processing Plant (ICPP) on the preparation and leaching of glasses from calcined alumina produced during 1964 in the fluid-bed calcination of highly radioactive wastes.[22,23] These wastes were treated in the Waste Calcining Facility (WCF) at the National Reactor Testing Station (NRTS), Idaho. Currently, this calcine is stored underground at the ICPP in stainless-steel bins that are located in concrete bins. Storage of the calcine in the stainless-steel bins is considered satisfactory at the NRTS. However, a more economical type of storage facility may be possible if the safety of long-term storage of calcines converted to glass can be assured. Work toward this end is in progress.

Alumina–phosphate glasses have been routinely prepared in the laboratory from plant-level-activity calcined alumina by using about 25 wt.% calcine, 16 wt.% PbO, and sufficient $NaH_2PO_4 \cdot H_2O$ to provide a glass containing 40 wt.% P_2O_5 and 19 wt.% Na_2O (Ref. 23). The calcine, lead oxide, and sodium orthophosphate are mixed dry in a porcelain crucible, heated at 400°C to remove water, after which the temperature is maintained at 900°C for about 16 hr. This laboratory work has shown that a high-quality, vitreous, homogeneous alumina–phosphate glass can be prepared from a radioactive fluid-bed calcine.

Samples of these glasses were then leached with distilled water at 25°C. The leach rate was 2×10^{-5} g/(cm^2)(day) after one week and slowly decreased to about 4×10^{-6} g/(cm^2)(day) after seven weeks. Cesium and strontium leached at about the same rate as aluminum, which suggested that their release was associated with dissolution of the glass. (However, at 95°C, cesium leached at a faster rate than the aluminum, whereas strontium leached more slowly than the aluminum.)

Leaching rates in distilled water at 25°C for the WCF alumina calcine and the alumina–phosphate glass were compared in terms of the percent of fission product leached per unit time. In a seven-week period, 80% of the ce-

sium and 40% of the strontium were leached from the calcine, and only about 0.005% of the cesium and 0.005% of the strontium were leached from the glass. Since alumina–phosphate glass stored in large volumes would undoubtedly have a lower ratio of surface area to weight than the small test specimens, much smaller percentages of fission products would be leached.

Irradiation up to a total dose of 10^{10} r does not cause devitrification of the alumina–phosphate glass.[23,24] Heating the glass for 30 days at 450°C results in thorough devitrification.[23] However, this devitrification does not increase the leaching rate with distilled water at either 25 or 95°C, provided a good vitreous glass is formed initially by using the correct composition, by fusing until the glass is homogeneous, and by thorough annealing.

Heat Dissipation from Waste-Solids-Storage Facilities

Currently, the highly radioactive calcined alumina from the WCF is being stored in facilities[25] that provide for cooling to remove fission-product decay heat. Waste-management costs could be reduced appreciably if radioactive waste solids such as fluid-bed calcines could be stored at shallow depths within a containment structure having a simplified (or possibly no) cooling system.[26] At the ICPP a program has been initiated to study the factors that affect the transmission of heat through soil. The various phases of the program include the following:

1. Evaluation of the physical properties of the local soil which affect heat transfer
2. Development of a mathematical model that describes the heat transmission in the buried heat-source–soil system
3. Preparation of a computer program for solving the equations derived from the model
4. Determination of the accuracy of the model by comparing the calculated temperature of the soil with the soil temperatures obtained in the vicinity of a buried electrical heat source
5. Verification of the mathematical model by comparing calculated temperatures with those obtained from the actual burial of a radioactive source

The electrical simulation of the buried source–soil system is in progress. The experimental apparatus consists of a 1500-watt electric heater buried 10 ft below the surface of the soil. Data on the moisture content and temperature of the soil are being obtained. In experiments with power to the heater of 950 watts, the moisture content of the heated soil was determined at various depths in three core holes located on a triangular pitch around the heater. Data from these determinations indicate that the soil moisture content is not affected in the vicinity of the core holes.

A mathematical model describing the heat transfer through the soil surrounding the buried heater has been developed. Preliminary comparison of the calculated temperatures with experimental temperatures indicates general agreement between the two.

Final Disposal

In-Tank Solidification

At PNL it is planned to utilize existing underground tanks for permanent storage of intermediate-level-activity plant wastes that have been concentrated to a salt cake (up to 16 ft thick) by in-tank evaporation.[27] As a means of achieving the evaporation, PNL proposes the use of electric heaters directly immersed in the waste.[28,29] Their use is expected to reduce the cost of future in-tank solidification units. In-plant tests of prototype electric heaters are under way. (The prototype heaters were selected on the basis of pilot-plant and semiworks-scale tests of the immersion heater concept. The results of these tests are presented in a report by Dunn at PNL.[30])

In support of the in-tank solidification process, work is continuing on computation of the temperature reached as a result of heat-generating fission products in the solid cake from Purex-plant wastes.[15,27] In previous calculations a 60-ft radius of insulation around the waste tank and 120-ft center-to-center spacings between tanks had been assumed. In recent calculations, however, a 300-ft insulated radius around the tank was assumed. These new calculations have given results which approximate a solitary tank with no tanks nearby.[15] This situation is useful for analyzing temperatures in tanks in which unusual conditions are present.

In Fig. IV-4, temperature profiles are presented for a horizontal plane through the center

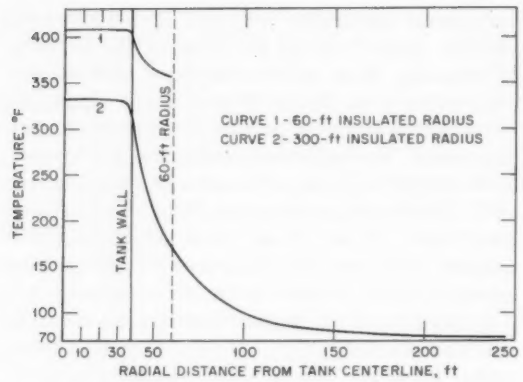

Fig. IV-4 Temperature profile in the horizontal plane of maximum temperature.[15]

Soil thermal conductivity, Btu/(hr)(sq ft)(°F/ft)	0.15
Cake thermal conductivity, Btu/(hr)(sq ft)(°F/ft)	0.80
Vapor thermal conductivity, Btu/(hr)(sq ft)(°F/ft)	200
Heat-generation rate, Btu/hr	3×10^4

of a 2-ft-thick cake generating 32,800 Btu/hr. In the cake of the tank with a 60-ft insulated radius, the maximum temperature is 408°F, and in the cake of the solitary tank, it is only 332°F. The close approach to ambient temperature (70°F) at radii greater than 200 ft shows a good approximation to a single tank in a medium of infinite radius.

In Fig. IV-5 the vertical temperature profiles along the axis of the tank in the two systems

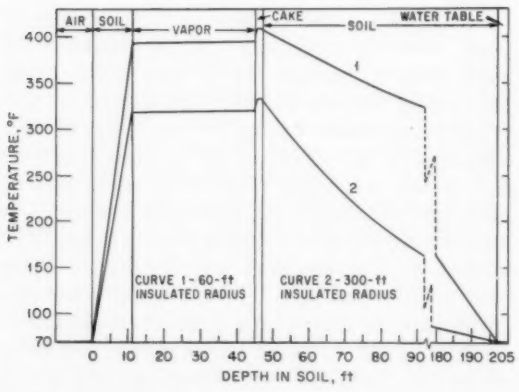

Fig. IV-5 Vertical temperature profile at the axis of the system.[15]

are compared. The temperature gradients toward the surface and the water table are quite similar, although much more heat flows radially in the larger system. For the tank with the 60-ft insulated radius surrounding it, about 86% of the heat generated goes to the atmosphere and the remainder goes to the water table. For the solitary tank, about 66% of the heat is distributed between the atmosphere and the water table within the 60-ft radius, and the remainder is dissipated beyond this radius.

Disposal by Hydraulic Fracturing into Shale

At ORNL, plans are being made to dispose of the intermediate-level-activity aqueous wastes into bedded shale by means of a hydrofracturing technique.[31] This method consists of first mixing the waste solution (up to 100,000 gal in injection tests) with cement and other additives and then injecting under high pressure the resulting grout through a specially constructed well into shale formation located at a predetermined depth (between 700 and 1000 ft below the surface). Sufficient force is exerted from the high-pressure injection to fracture the shale strata. The grout flows into the cracks to form thin horizontal layers several hundred feet across where it solidifies to fix the radioactive wastes in the formation. An injection plant was built and a series of five injections was made to test the operation of the equipment, the performance of the mix, and the underground behavior of the grout sheets. Core samples of the grout sheets from these injections have been obtained and analyzed.[32,33] The analyses showed the following: (1) The grout is denser and stronger than laboratory-prepared grout samples with an equivalent composition. (2) Considerable underground mixing occurs during an injection between the grout that is injected first and that injected last. (3) The amount of cement in a mix can be reduced (thereby reducing the cost) without adversely affecting the mix. (4) The injected radionuclides are well fixed in the grout. However, during the coring of the grout sheet from the third injection, a backflow of several thousand gallons of water containing a trace of ^{137}Cs was noted; this resulted from improper control of mixing during the injection and subsequent separation of water from the grout. No flow of water was observed during the

coring of the grout sheets from the fourth and fifth injections.

A sixth injection test was completed with a less expensive cement mix in which some of the portland cement was replaced by Kingston fly ash.[34] About 64,000 gal of an ORNL plant waste was injected. Coring of the grout sheets and bleed-back tests to evaluate phase-separation qualities of the mix are in progress. Following the evaluation of the results of this test, the injection plant will be modified to carry out routine disposal of ORNL waste.[33,35,36]

Fission-Product Recovery

ORNL Solvent-Extraction Studies

At ORNL, laboratory development of solvent-extraction processes for recovering various fission products from a variety of waste solutions has continued.[37]

CESIUM

Previous work had shown that cesium could be successfully removed from alkaline solutions by a process (Phenex) that involved extracting the cesium with substituted phenols and then stripping it with dilute acid.[38] Nearly all recent test work has been done with 4-*sec*-butyl-2-α-methylbenzyl phenol (BAMBP), which is highly selective for cesium.[37] Batch tests with 1*M* BAMBP in Amsco 125-82 have further confirmed this selectivity when contaminant metals not previously tested (calcium, barium, molybdenum, and technetium) were not extracted from simulated alkaline wastes consisting of sodium nitrate, sodium tartrate (added as complexing agent), and cesium and with *p*H adjusted to 11.7. Coefficients of extraction for the contaminant metals were all less than 0.01 and that for cesium was 3. It was previously shown that BAMBP had good radiation and chemical stability under conditions expected for the cesium recovery flow sheet.[39] However, when BAMBP was contacted for long periods (four days) with nitric acid (0.1*M*) solutions containing nitrite ion (0.1*M*), the BAMBP was extensively degraded and the cesium extraction coefficient was reduced[37] to a very low value (0.09). (This degradation of BAMBP had also been observed by workers at Hanford.) Nitrite could possibly be introduced into the nitric acid stripping system by entrainment of the aqueous waste solution (which is high in nitrite ion) in the organic extract and by radiolytic decomposition of nitric acid in the stripping system. Studies showed that adding a small amount of sulfamic acid to the strip solution destroyed the nitrite and thus prevented attack of BAMBP.

CERIUM AND PROMETHIUM

Studies were continued of methods for the separation of cerium and promethium from the mixture of rare earths derived from a three-cycle solvent-extraction process[40] for recovery of fission products. It was previously shown that cerium could be separated from other rare earths when it was oxidized with silver-catalyzed potassium persulfate and then extracted[39] with di-2-ethylhexyl phosphoric acid (D2EHPA). Good recoveries were obtained only when the oxidation step was performed at elevated temperatures, with the solvent phase present and with a nitric acid concentration in the aqueous feed of 1.3*M*. In recent tests the maximum oxidation rate occurred with about 2*M* HNO_3 in the aqueous phase.[37] At this acidity, nearly complete oxidation can be achieved with the solvent phase absent. This procedure is preferred since it prevents prolonged contact of the solvent with the hot oxidizing solution. More than 98% of the cerium from a mixed-rare-earth feed (0.005*M* in cerium) was oxidized and subsequently extracted with 0.3*M* D2EHPA in Amsco 125-82 in 20 to 30 min at 60°C, with the use of 1.8 moles of potassium persulfate per mole of cerium.

The separation of promethium from the other rare earths (after cerium removal) was studied with several types of solvent-extraction reagents.[37] The best results were obtained with tributyl phosphate (TBP) and D2EHPA. The TBP was previously used in a flow sheet developed for the small-scale recovery of promethium from concentrated nitric acid.[41] Recent batch studies with TBP indicated that this flow sheet could be modified to make the process more attractive for large-scale use. This improvement could be accomplished with a modest increase in the number of stages (a 20-stage mixer–settler unit had been previously used), which would thereby allow greatly reduced flows of TBP and scrub acid per unit of promethium. In work with D2EHPA, test results were promising. Separation factors of about 2.5 between adjacent rare earths were obtained with this extractant at relatively low (0.2*M* to 0.4*M*) nitric acid concentrations in the extraction and scrubbing systems. The process appears to

have an appreciable advantage over the TBP–nitric acid process because separation factors are higher and the required aqueous-phase acidity is much lower (0.3*M* vs. 12*M* HNO_3). Demonstration runs in mixer–settler equipment are planned to verify the feasibility of the process.

RUTHENIUM

A tentative process was outlined for recovering ruthenium[37] from acid Purex wastes (1WW). In the process, developed with simulated 1WW, ruthenium was satisfactorily extracted with a tertiary amine and then stripped with dilute caustic solution. Hot-cell tests of this process with actual pilot waste are planned.

STRONTIUM, CESIUM, AND RARE EARTHS

The fission-product recovery processes which were originally developed for treating Hanford Purex-plant wastes and which employ D2EHPA for an extractant[42] are being studied for application to wastes that contain dissolved stainless steel (Darex process) or large amounts of aluminum nitrate (TBP-25 process).[37] In batch tests with simulated stainless-steel wastes complexed with sodium tartrate and sodium diethylenetriaminepentaacetate, strontium, cesium, and rare earths were effectively removed. In other batch tests with a simulated TBP-25 process waste (1.7*M* aluminum ion) complexed with relatively large amounts of sodium tartrate and adjusted for *p*H with sodium hydroxide, strontium and cerium extractions were demonstrated.

Other Literature

In two recent review articles, the management of radioactive wastes is described.[43,44] The nature of the wastes is outlined, and the techniques for handling them are presented. Economic aspects of the treatment of low- and high-level-activity wastes are discussed.

A new annual publication, Waste Management Research Abstracts, is being published by the International Atomic Energy Agency, Vienna, Austria.[45] This publication will serve as a means for disseminating information on national waste-management research programs. The first issue contains abstracts of research projects which were completed in 1963 and 1964 by Czechoslovakia, the Federal Republic of Germany, Italy, Japan, Sweden, United Kingdom, United States, and Union of Soviet Socialist Republics. The abstracts include reports of a large number of projects which previously were either not published or were published with restricted distribution.

At the Shippingport Atomic Power Station, spent radioactive ion-exchange resin from the operation of the reactor is stored in two underground tanks. After about seven years of plant operation, the tanks had become full; it then became necessary to dispose of the resin to provide additional storage space. Suchoza[46] describes the procedure followed and the equipment utilized for transferring the spent resin from the two tanks to concrete-shielded steel shipping containers, which also served as the ultimate burial vessels. Some 2500 cu ft of spent resin was pumped into five shipping containers, after which they were shipped by rail to the burial site. The entire cost of the operation was about $40 per cu ft of radioactive waste removed; included in this cost were equipment procurement and installation, operations, shipment, and burial.

Tharin[47] at Savannah River describes a computer program, TAFI-II, which was written in FORTRAN II to assist in the regulation and inventory control of radioactive fission products that are stored in the waste tanks at Savannah River. The inventories and heat-generation rates are computed for 13 isotopes in each of 24 waste tanks. The program prepares a report that summarizes the data and provides an up-to-date status of the conditions in a waste tank.

Japanese workers[48] have summarized their laboratory-scale investigations of an evaporation process applicable to the treatment of low- or intermediate-level-activity wastes. This process consists in preconcentration of the waste in a conventional type evaporator followed by final evaporation and conversion to solid of the evaporator concentrate in a spray-fed fluid-bed calciner. The operational characteristics of fluid-bed reactors were studied in small-scale units in which nonradioactive solutions were spray-fed. The mechanism of heat transfer in a fluid bed was also investigated, and engineering data were obtained and correlated.

Godfrey[49] describes a countercurrent crystallization system that almost eliminates the problem of solids handling and permits multiple stages of crystallization without requiring the separation of crystals and supernatant following

each stage. Such a system would have application in the Redox solvent-extraction process where aluminum nitrate nonahydrate (ANN) is used as a salting agent. The ANN would be separated from fission products and recovered, for recycle, from the Redox-plant waste. (The recovery of ANN would also make it possible to reduce plant waste volumes and to recover and isolate high specific heat fission products.) This process is capable of achieving decontamination factors up to 10^5 by the use of 12 to 15 stages. The author discusses in detail the development of the process (laboratory- and bench-scale work) and a mathematical model for the process system. Since the countercurrent crystallization concept has potential application in other systems, he has presented the variables investigated in a graphical form to aid in the design of these systems.

At ORNL two processes have been successfully investigated for the treatment of low-level-activity wastes. One is a recycle scavenging–precipitation ion-exchange process.[50] King and Ichikawa[51] have summarized the pilot-plant runs that were made to demonstrate this flow sheet. These runs showed that strontium and cesium activity levels can be reduced by factors of about 1000 at a cost of about 75 cents/1000 gal in a 750,000-gal/day plant. The other is a scavenging–precipitation foam separation process.[52] Davis, Kibbey, and Schonfeld[53] discuss the laboratory-scale runs conducted to demonstrate this process and the work involved in the development of the process flow sheet. In work related to the foam-separation portion of this process, Haas[54] reports on the experimental engineering studies that were conducted to determine how to design and to operate an efficient foam column.

The heat-generation rate of highly radioactive (~20 curies/lb) WCF alumina calcine produced from ICPP wastes was reported in the Fall 1965 issue of *Reactor Fuel Processing*.[55] The equipment (lead-constructed calorimeter) and the experimental procedures used for heat-generation measurements are described in detail in a recently issued report by Rhodes and Jacobson.[56] The heat-generation rates for the calcines produced from two different ICPP wastes were 0.343 and 0.303 Btu/(hr)(lb). The measurements made with this equipment were estimated to be within 2% of the true value. An accurate value for the heat-generation rate must be known in order to design storage bins for the calcine.

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Section V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Production of Uranium Oxides

By J. J. Barghusen

Reduction of Uranium Oxides

The principal method for the production of UO_2 involves the reduction of higher uranium oxides, UO_3 or U_3O_8, by a gaseous reducing agent. Thus an understanding of the phase changes and kinetics of these reactions is of fundamental importance. To provide an insight into the mechanisms governing reduction processes with uranium oxides, Vlasov and associates[1] have studied the reduction of UO_3 at 470°C and U_3O_8 at 700°C by solid carbon. Amorphous UO_3 reacts directly with carbon (graphite) to produce carbon dioxide gas. The phase changes accompanying the reduction of UO_3 can be represented as

$$UO_3 \rightarrow UO_{2.91} \rightarrow U_3O_8 \rightarrow U_3O_{8-z_{max.}}$$

The first step proceeds without formation of a new phase in that the step involves only the removal of oxygen from solid solution. Subsequent steps are accompanied by formation of new crystalline phases. It was observed that the extent of UO_3 reduction decreases with an increase in CO_2 pressure. Although the interaction of carbon with UO_3 leads to the formation of some CO, the small quantity of CO formed reacts rapidly with UO_3 at 470°C; therefore CO_2 is the only observed oxidation product.

The reduction of U_3O_8 by graphite at 700°C is accelerated both by an increase in the pressure used to form compacts of U_3O_8 and graphite powder mixtures and by an increase in the CO_2 pressure. Increase of the CO_2 pressure accelerates the gasification of carbon by CO_2 which is the slowest step in the reduction of U_3O_8 by carbon. Increase of the compacting pressure of the reduction mixture also seems to accelerate this step, since the resulting deformation of the graphite lattice increases with increased contact between the reactants, in particular as the result of formation of surface complexes and dissolution of the oxide oxygen in carbon.

In other work, Beketov and Vlasov[2] investigated the kinetics of the dissociation of gamma UO_3 in vacuum at temperatures of 600 to 675°C. At these temperatures gamma UO_3 dissociates by stages: first to give a U_3O_{8+x} phase, and then to form U_3O_8. Dissociation of gamma UO_3 begins at a low rate, which then increases as the process proceeds and reaches a maximum when the overall composition of the solid phases is $UO_{2.90}-UO_{2.88}$. On further decrease of the oxygen content in the solid phases, the dissociation rate decreases rather slowly at first, and only when the composition $UO_{2.79}-UO_{2.77}$ has been reached does the rate decrease sharply with increasing dissociation. At a solid-phase composition of $UO_{2.67}$, the rate becomes virtually zero. It was observed that the apparent activation energy of dissociation depended on the degree of dissociation, being 42.5 kcal/mole at the initial stage of the process and 60.5 kcal/mole as the composition of the solid phase approached U_3O_8. In a recent publication, Beketov et al.[3] reported that, at 525 to 600°C, beta UO_3 associates to give first a U_3O_{8+z} phase and finally U_3O_8.

On the basis of the results of high-temperature X-ray photography and a critical survey of previous work, Rachev, Kovba, and Ippolitova[4] have constructed a phase diagram of the UO_2-UO_3 system. Uranium oxide samples of various compositions were prepared when mixtures of UO_2 and U_3O_8 were annealed at 1000°C for 20 hr in sealed quartz ampoules. X-ray data were obtained from exposures made with a high-temperature camera in the ranges 850 to 1150°C

(for $UO_{2.02}$–$UO_{2.40}$) and 20 to 1000 °C (for $UO_{2.50}$–$UO_{2.667}$).

Conversion of Uranium Hexafluoride to Uranium Dioxide

A process for the direct conversion of uranium hexafluoride to high-density uranium dioxide has been developed at Oak Ridge National Laboratory (ORNL).[5,6] The process involves the reaction of UF_6 with a mixture of hydrogen and oxygen or steam as follows:

$$UF_6 + 2H_2O + H_2 \rightarrow UO_2 + 6HF$$

The factors that favor direct reduction to UO_2 were: (1) low system pressure, (2) temperatures sufficiently high to limit formation or condensation of possible intermediate compounds, and (3) excess amounts of both hydrogen and oxygen or steam to drive the reaction to completion. Demonstration tests of the process were performed in a tube furnace containing a water-cooled gas-injection system and a cylinder of low-density alumina on which the UO_2 product was deposited (Fig. V-1). A blanket of argon

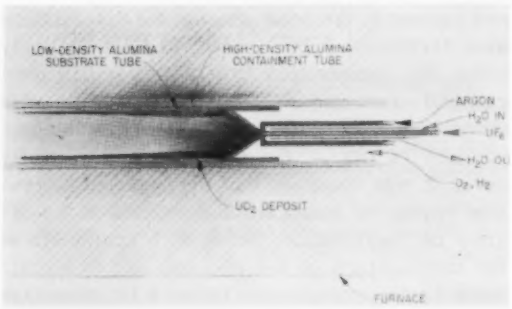

Fig. V-1 Arrangement of water-cooled injector for introducing uranium hexafluoride.[5]

was supplied at the tip of the injector to separate the reactants and thereby prevent deposition of UO_2 on the injector.

In the temperature range of 1200 to 1500 °C and with the system pressure below 10 torrs, UO_2 is formed when the gas-composition limits are held within 60 to 80 vol.% H_2, 10 to 40 vol.% O_2 or steam, and 1 to 10 vol.% UF_6. Dendritic crystalline UO_2 is obtained with a gas composition of 78 vol.% H_2, 20 vol.% steam, and 2 vol.% UF_6 at 6 torrs and 1250 °C. Deposits of this type have oxygen-to-uranium ratios of 2.000 to 2.003 and fluorine contents of less than 10 ppm. The dendritic crystals are easily removed from the alumina substrate and are readily crushed to a powder.

A dense uniform deposit of UO_2 is obtained when the system pressure is reduced to 2 to 3 torrs and the UF_6 content of the gas is increased to greater than 3 vol.%. In demonstration tests, UO_2 was deposited on the alumina substrate at a rate of 6 mils/hr. Bulk densities of the deposit, measured by alcohol immersion, ranged from 10.96 to 11.04 g/cm^3.

The stoichiometry of the oxide product was affected by changes in the feed-gas composition. Increasing the oxygen content of the gas, in general, resulted in an increase in the oxygen-to-uranium ratio in the product. Oxygen-to-uranium ratios were found to be constant along the length of the deposit. Raising the system pressure above 20 torrs yielded UO_2F_2 powder under conditions that produced only UO_2 at lower pressure. Operation at temperatures above 1300 °C resulted in no significant advantage.

Ukaji and Wada[7] have been issued a patent on a one-step process for preparing UO_2 from UF_6. The major feature of the patent is the method employed to mix the UF_6 and the reducing gas streams: UF_6 and a mixture of excess steam and hydrogen are simultaneously introduced, tangentially and in opposition to each other, into the upper portion of a vertical reaction tube at 500 °C. The product gases are removed from the top of the reaction vessel, and the solid UO_2 product is collected at the bottom of the vessel. Uranium dioxide prepared by this method was shown to be highly reactive toward HF to produce UF_4. Analyses showed the UO_2 to contain less than 0.01 wt.% UO_2F_2.

Production of Thorium Dioxide by a Sol-Gel Process

Dense particles of ThO_2, which are suitable for vibratory compaction into tubes and have a bulk density approaching 90% of theoretical, have been prepared at ORNL by a sol-gel process.[8-10] The process involves four major steps (see Fig. V-2): (1) drying and denitration

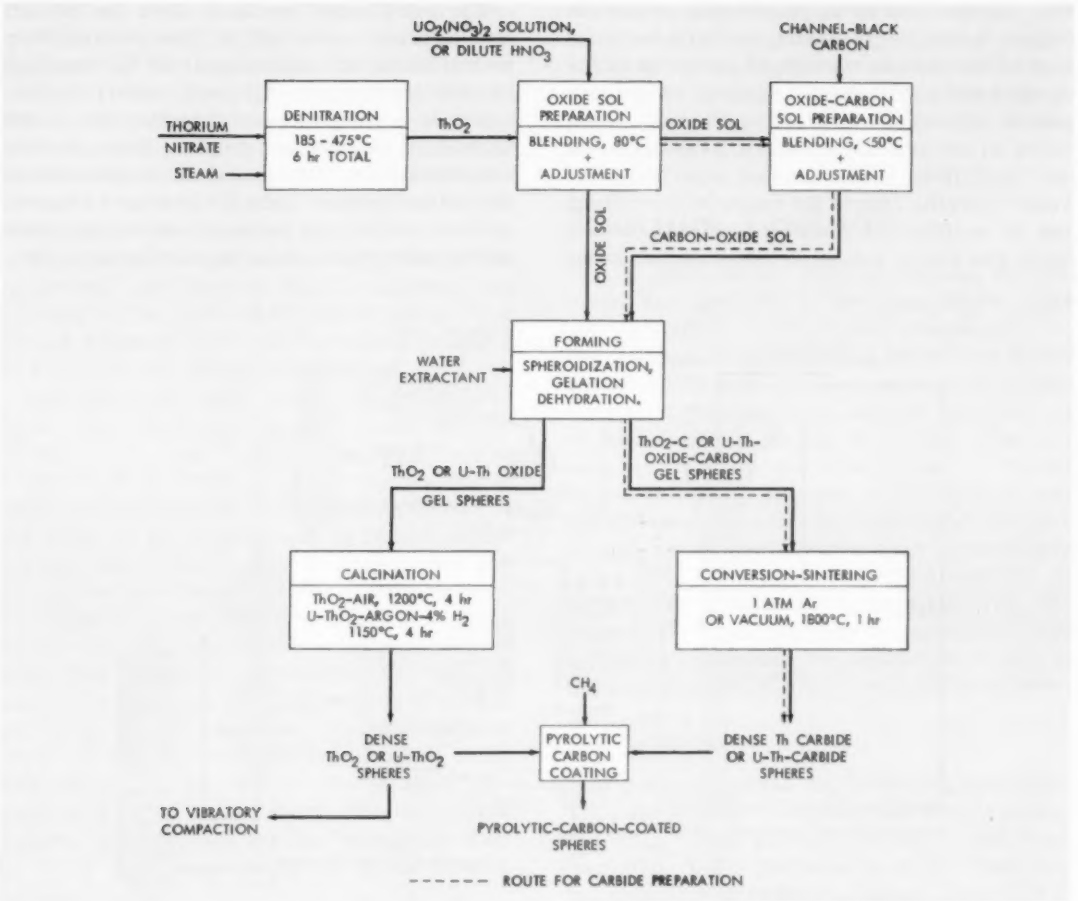

Fig. V-2 Sol-gel process for preparation of dense spheres of uranium–thorium oxides or carbides.[6]

of thorium nitrate to ThO_2, (2) dispersion of the oxide to a hydrosol, (3) conversion of the sol to a gel by extraction of the water into an organic solvent, and (4) calcination of the gel spheres to dense ThO_2 particles. The same process steps, with slight modifications, can be applied to the production of (Th,U)O_2, ThC, or (Th,U)C spheres.

The previous sol-gel flow sheet incorporated a low-temperature drying step for the conversion of the sol to a gel. Details of this process step and of steps 1 and 2 were reported in a previous issue of *Reactor Fuel Processing*.[11] Recent work[8-10] has concerned the development of a method for converting ThO_2 sol to a gel based on the dispersion of the sol in an organic drying agent. The process involves the jet dispersion of sol from a two-fluid nozzle into a liquid that has negligible solubility in the sol; moderate capacity for dissolving water; and negligible tendency to extract thorium, uranium, or carbon from the sol. Slow extraction of water from the sol microspheres leads to strong gel miorospheres which can be handled, further dried, and finally fired to dense spheres.

A schematic diagram of the equipment used to produce gel spheres in the size range 100 to 1000 μ is shown in Fig. V-3. The facility consists of a tapered fluidizing column (2-in.-minimum diameter, increasing to 3 in. in diameter over a 40-in. height), wherein the sol droplets are partially dehydrated by contact with 2-ethyl-1-hexanol, and a solvent recovery system for removal of water from the solvent which is then recycled. Three organic streams enter the bottom of the column and flow upward through

the column. One of these streams enters the column tangentially, creating a swirl in the lower half of the column; the second stream is introduced axially. The mixing induced by the tangential stream prevents accumulation of particles on one side of the column. If the tangential and axial flows are controlled separately, the velocity profile across the center of the column can be modified. A flattened profile is desired since this allows wet sol drops to remain in the upper half of the column. The third organic stream is introduced as the dispersing fluid in the two-fluid nozzle through which the aqueous sol is fed to the column. The aqueous sol is metered by a syringe pump to the two-fluid nozzle and dispersed into droplets. These droplets fall through the upflowing organic until their velocity approaches the fluidizing velocity. As water is extracted from the aqueous droplets, the sol sets to a rigid gel. The denser gelled particles require a higher fluidizing velocity and thus gradually fall through the tapered column and collect at the bottom. The time required for gelation ranges from 2 to 20 min, depending on the initial molarity of the sol and the initial drop size.

The wet alcohol overflows from the column into a holdup tank and is then metered to a steam-heated still operating at 150°C. The dried alcohol (containing ~0.5 wt.% water) is collected in a reservoir and then recycled. In the course of forming sol droplets from nitrate-stabilized sols, nitric acid is extracted into the alcohol phase. Since the presence of accumulated nitrate ion in the alcohol might cause undesirable oxidation of the microsphere, several methods for removing nitrate from the alcohol are being investigated.[10] The use of a hydroxide-form ion-exchange resin was unsuccessful, since thoria microspheres prepared by use of alcohol treated by this method did not densify at the normal calcination temperature of 1150°C. An aqueous scrubbing technique is now being evaluated as an alternative method.

The design of the nozzle for dispersing the sol has been paramount in achievement of spherical gel particles of uniform size. A two-fluid nozzle was developed to avoid the undesirably small orifice sizes required for free-fall drop formation. In this design the aqueous sol is introduced in the center of the flowing organic stream. The continuous sol is accelerated to the velocity of

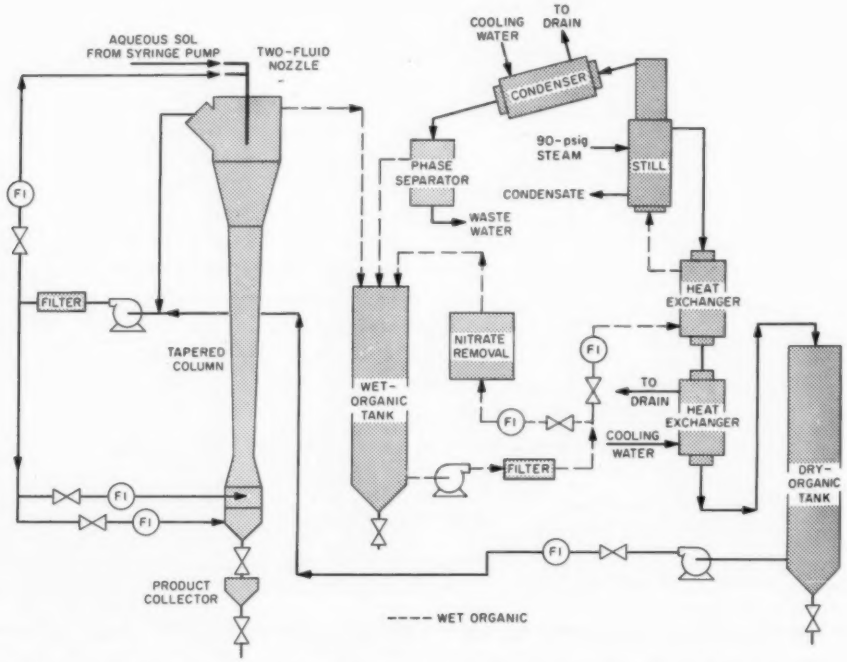

Fig. V-3 Column for forming gel microspheres and system for recovering solvent.[10]

the organic and breaks up to give sol droplets with diameters 2.0 to 2.5 times the minimum diameter of the sol stream. If production of uniformly sized droplets is to be assured, the flow of the organic phase must be laminar and the sol should be injected in such a manner as to minimize disturbances. A 10-in.-long nozzle is used to ensure good droplet formation before discharge into the tapered column.

A surfactant is dissolved in the organic phase to prevent sol droplets from coalescing and sticking to the walls of the glass column. The use of Ethomeen S-15, in concentrations of 0.1 to 0.5 vol.%, has proved satisfactory.

Demonstration tests employing organic recycle have been performed[9,10] in this facility by the use of a feed stream containing 3*M* sol at a rate of 230 g of ThO_2 per hour. The quantity of water removed by the still represented 85% of the water in the original sol. As recycle of the organic was continued, it was observed that the alcohol darkened slightly, and particle clustering began to occur. The tendency toward clustering was eliminated by the addition of surfactant. The apparent degradation or loss of surfactant with time and the presence of nitrate ion in the organic phase may present problems if the alcohol is to be recycled for a long time. The density of the thoria spheres after calcination to 1150°C was nearly the theoretical density. Spheres with average diameters of up to 750 μ have been produced in the tapered column.

Preliminary experiments have been performed to determine methods for controlling the porosity of thoria or $(U-Th)O_2$ particles produced by the sol-gel process.[10] Two methods have been investigated: (1) A carbonaceous material (lampblack) was blended in the sol prior to gel formation. On drying and firing, the carbon was oxidized to CO or CO_2, thereby generating holes whose size and number was a function of the type and amount of carbonaceous material added. (2) Incomplete firing was used, thereby retaining porosity within the particles which might otherwise be sintered out in complete firing of the particles.

Cogliati, Lanz, and Mezi at Comitato Nazionale per l'Energia Nucleare have described the application of sol-gel techniques for the preparation of UO_2 or $(U-Th)O_2$ particles.[12] The process is basically similar to that developed at ORNL. Gelation of the sol droplets is attained by dispersion of the sol within a high-molecular-weight alcohol immiscible with water. Extraction of the nitric acid from the sol is achieved by addition of an anionic liquid exchanger (such as Primene) to the organic phase. The time required for gelation is approximately 15 min.

Thorium Carbide

In a study of the reaction between thorium metal and graphite in the temperature range 900 to 1600°C, Takeuchi and associates[13] observed that, at temperatures below 1200°C, the reaction rate was parabolic with an activation energy of 53 kcal/mole. Marker experiments showed that the growth of carbide film was mainly due to the migration of carbon, and the rate-determining process of the reaction was the diffusion of carbon through the carbide film formed on the metal surface. At temperatures below 1200°C the reaction product was ThC. At higher temperatures the ratio of ThC/ThC_2 decreased with increasing temperatures. The activation energy for the formation of ThC_2 at temperatures above 1300°C was 120 kcal/mole.

Sol-Gel Process

A sol-gel process for preparing spheroidal ThC_2 and $(U-Th)C_2$ particles has been developed at ORNL.[8,14] The process consists of four steps (see Fig. V-2): preparation of the oxide sol, incorporation of carbon in the sol, formation of gel spheroids, and firing of the spheroids. The oxide sol is prepared by dispersing thoria in dilute nitric acid at 80°C. Carbon black (mean particle size of 130 A) is fixed into the sol to give an oxide–carbon sol having a carbon-to-metal atomic ratio of at least 4 to 1. The oxide–carbon suspension is stirred vigorously for about 1 hr at 50°C to disperse and blend the mixture thoroughly and produce, for practical purposes, an oxide–carbon sol. Actually, the result is not a true sol, because appreciable aggregation and settling will occur if the system is allowed to stand without agitation.

Formation of the gel is achieved by dispersion of the oxide–carbon sol in an organic liquid. Initial work[14] was performed with solutions of CCl_4–isopropyl alcohol containing 15 vol.% alcohol. Successful tests have recently been performed[8] in the facility shown in Fig. V-3 with the use of 2-ethyl-1-hexanol as the organic extractant. It has not been established

that surfactants are necessary to prevent coalescence and wall sticking of the gel droplets, since carbon itself may be a sufficiently active surfactant.

The gel spheroids are dried and then converted to the dicarbide by heating either in vacuum or in argon. Essentially complete (>99%) conversion of the oxide to the carbide may be attained in 1 to 6 hr in the temperature range 1500 to 1750°C.

Conversion of Thoria to Dicarbide in Rotating Crucible

Workers at ORNL have prepared[5] dense particles of ThC_2 or $(U-Th)C_2$ from dense sol-gel ThO_2 or $(U-Th)O_2$ microspheres by dispersing the spheres in graphite flour or lampblack and heating the mixture in a graphite crucible for 2 hr at 2200°C and 1×10^{-2} torr. Rotating the crucible at over 15 rpm made it possible to avoid reaction bonding of the ThO_2 particles to the crucible and agglomeration of the particles at temperatures greater than 2000°C. Studies with a rotating crucible showed that conversion of 300- to 400-μ-diameter ThO_2 microspheres to ThC_2 could be achieved in 5 hr at 2050°C, 3 hr at 2150°C, 2 hr at 2200°C, and at most 1 hr at 2300°C. The product obtained at 2300°C was highly agglomerated and contained large holes.

Coating of Thorium Dicarbide Particles

Thorium–uranium dicarbide is extremely reactive to moisture. Fuel compacts containing $(Th-U)C_2$ disintegrate by hydrolysis after a few hours of exposure to air. A process for coating $(Th-U)C_2$ particles with carbon films to protect the carbide against attack by water is being developed at ORNL.[5] Development studies on coating methods are being performed in fluidized-bed reactors and rotary drums. A description of the ORNL high-temperature fluidized-bed particle-coating apparatus appeared in a previous issue of *Reactor Fuel Processing*.[15] Preliminary studies on the use of rotary drums have concerned observations on the motion of particles within the drums.[5] Experiments have shown that nearly spherical particles remain practically motionless in a smooth horizontal rotating drum until the charge depth reaches a certain value. When the depth of charge is increased, the particles tumble in a random motion. This observation indicates that baffles must be employed in drums to increase particle agitation and gas–solid contact. On the basis of these studies, a prototype rotary-drum coater for operation up to 2200°C has been designed.[5]

Phase Diagrams in the Thorium–Carbon Systems

Since thorium carbide systems are becoming of increasing technical importance in the development of nuclear reactors, knowledge of their physical properties is of practical interest. The results of an extended investigation of the thorium–carbon system over the composition range 5 to 15 wt.% carbon has been reported by Henney and Jones.[16] Thorium dicarbide undergoes two polymorphic transformations, changing from monoclinic to tetragonal at 1410 ± 20°C and from tetragonal to cubic at 1500 ± 20°C. When ThC is present, the temperature of the monoclinic-to-tetragonal transition is lowered to 1290 ± 20°C. A solid solution is formed between ThC and cubic ThC_2 at temperatures higher than about 2100°C.

Dilatometry and thermal-analysis measurements at ORNL[5] have shown that ThC_2 exhibits phase transformations at 1500 ± 25°C and at 1430 ± 10°C. Two similar transformations were observed for ThC_2–25 mole % UC_2. At 1768 ± 25°C, UC_2 exhibited a phase transformation. Two phase diagrams have been proposed for the UC_2–ThC_2 system.[5]

Production and Properties of Plutonium Dioxide

The role of plutonium dioxide in the production of plutonium metal or compounds for use in fast reactor fuels is that of a primary feed material. The standard feed for the production of PuO_2 or mixed $(U-Pu)O_2$ is a nitric acid solution of plutonium or uranium–plutonium. Sowden, Ainsley, and Stockdale[17] have reviewed the work carried out at Harwell on the preparation of UO_2-PuO_2 powders for nuclear fuels. Studies were made on the preparation of $(U-Pu)O_2$ powders by coprecipitation from U(VI)–Pu(IV) solution, a versatile method for preparing powders that sinter to a high density. However, the precipitates have poor handling properties. Alternative techniques were surveyed, particularly in relation to plutonium con-

tents of 15 wt.% and higher. Coprecipitation with oxalic acid from U(IV) – Pu(III) solution appears the most attractive alternative process.

In a study of the sintering behavior of mechanically blended $UO_2 - PuO_2$ mixtures, Houston observed that physical densities in excess of 90% of theoretical density can be readily achieved.[18] Plutonium dioxide was prepared by calcination of Pu(IV) oxalate in air for 0.5 hr at 760°C. The blended powders were fabricated into pellets without the use of binders and sintered in flowing 6 vol.% hydrogen–nitrogen at 1600°C. The results showed that solid solution is difficult to achieve by the blending and sintering techniques used in this study. Therefore differences in behavior as a nuclear reactor fuel may arise between pellets prepared from coprecipitated feed and those prepared by mechanical blending of component powders.

Workers at ORNL have developed a method for preparing PuO_2 microspheres by a sol-gel process.[10] Plutonium sols can be prepared by digestion of freshly precipitated $Pu(OH)_4$ in sufficient HNO_3 to provide an NO_3^-/Pu mole ratio of about 1. To produce dense oxides from the sol, the workers have found it necessary to reduce the nitrate content of the sol by drying the sol to a gel, heating the dried gel to remove nitrate, and suspending the dried gel in water to form a sol. Plutonium sols prepared by this method have NO_3^-/Pu ratios of between 0.08 and 0.13. Spectrographic analysis of plutonium-sol particles produced by digestion of the hydroxide with dilute HNO_3 have shown that the sol particles are polymers.

Microspheres of PuO_2 were produced when the low-nitrate sol (100 g of plutonium per liter) was slowly fed into an agitated mixture of 2-octanol and 2-methyl-1-pentanol. The particle sizes of the PuO_2 spheres obtained after calcination at 1150°C varied from 5 to 40 μ. More uniform-size spheres were obtained by the use of a tapered column. Plutonium dioxide and $PuO_2 - ThO_2$ spheres having a particle size 200 ± 20 μ were produced in the tapered column (see Fig. V-4). Satisfactory spheres (sintered density, 97 to 99% of theoretical density) have been prepared from $PuO_2 - ThO_2$ sols containing 2 to 50 wt.% PuO_2. The drying rate of PuO_2 sol achieved with a mixture of 2-octanol and 2-methyl-1-pentanol was excessive; and hollow, broken spheres were produced. Much more satisfactory results were obtained in subsequent tests by use of a mixture containing 59.6 vol.% 2-ethyl-1-hexanol, 40 vol.% 2-octanol, and 0.4 vol.% Amino-O.

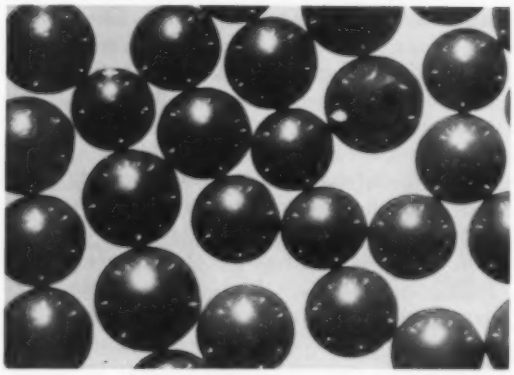

Fig. V-4 $PuO_2 - ThO_2$ microspheres calcined at 1150°C; diameter, 180 to 210 μ (Ref. 10).

Production and Refining of Plutonium Metal

Plutonium metal has been prepared on a laboratory scale by the direct reduction of plutonium dioxide with liquid magnesium–zinc alloy in the presence of fluxes composed of alkali and alkaline-earth halides.[19] Over 99% reduction of PuO_2 was achieved in 0.5 hr at 800°C with 5 to 10 wt.% magnesium–zinc alloy. Alloys containing higher magnesium concentrations resulted in incomplete reductions. Rate of reduction of PuO_2 was essentially independent of flux composition. However, the extent of PuO_2 reduction was limited by the destruction coefficient of plutonium between the salt and metal phases. Salts with low magnesium chloride concentrations (<50 mole % $MgCl_2$) are preferred, since the plutonium distribution to the salt decreases with decreasing magnesium chloride concentration.

A program to demonstrate the continuous production of plutonium metal by electroreduction from a fused chloride salt is under way at Hanford Atomic Products Operation.[20] The process involves feeding of $PuCl_3$ into a melt consisting of 28 wt.% $BaCl_2$, 42 wt.% KCl, and 30 wt.% $PuCl_3$ and electrodepositing molten plutonium at 800°C at a cathode. A detailed description of the process and equipment was

presented in a previous issue of *Reactor Fuel Processing*.[21] Recent work[20] has concerned a study of scale-up problems and the design of a cell suitable for a production process. It was demonstrated that the process is capable of handling a feed of $PuCl_3$ containing 10 to 20% unchlorinated material (oxide). Plutonium metal was obtained in a separate test from a PuO_2 feed material at 65% electrical efficiency.

In an investigation of the electrochemistry of Pu(III) in molten alkali chlorides, Nissen[22] observed there was no evidence that the cathode reduction of Pu(III) to the metal in a LiCl–KCl system passes through a stable lower oxidation state.

Fused-salt electrorefining processes have been developed at Los Alamos Scientific Laboratory for production of high-purity plutonium metal on a 500-g and 3.5-kg scale. Descriptions of the process have appeared in previous issues of this journal.[21,23,24] Recent development work on this process at Hanford[25] has indicated that the processing time can be significantly reduced by increasing the electrolysis rate from 70 to 125 g/hr and decreasing the time required for heatup and cooling. The increased electrolysis rate was realized by modification of the design of the electrolyte and molten-anode stirrer. A two-piece cell design provided the capability of shorter heatup and cooling periods. The process equipment was completely instrumented so that during demonstration tests there was no need to attend to the equipment once the electrolysis was started.

In the fabrication of plutonium metal, molten metal is cast in a precoated graphite mold. The coating (calcium fluoride) minimizes, but does not prohibit, attack of the graphite by plutonium. When the graphite molds are broken away from the casting, small quantities of plutonium metal adhere to the mold surface. Williams and Pinamont[26] investigated several methods for recovering plutonium from graphite residues. These methods include ignition of the graphite and recovery of the ash by dissolution, hydrochloric acid leach, fuming nitric acid leach, and nitric acid–fluoride leach. Of these methods, the use of a leach solution containing 12.5 *M* HNO_3 and 0.1 to 0.3 mole per liter of fluoride ion was found to be most effective. Leaching for 2 hr at reflux temperature was shown to be adequate for most dissolutions. Washing of the leached graphite was also found to be important for effective plutonium removal.

In the preparation of nuclear fuel materials, metallurgical scrap containing plutonium–uranium, plutonium–thorium, and plutonium–uranium–thorium materials is generated. Chemical development work is being carried out at Pacific Northwest Laboratory to test solvent-extraction flow sheets for separating plutonium from uranium and thorium. Results of testing of two flow sheets have been summarized in a recent report.[27]

Preparation and Properties of Uranium and Plutonium Nitrides

By P. A. Nelson

Uranium and plutonium nitrides are usually prepared by reaction of nitrogen with the metals or their hydrides. For commercial-scale preparation of the nitrides, however, UO_2 and PuO_2 would be less expensive feed materials than the metals, and consideration is being given to methods of converting the oxides to the nitrides.

A thermodynamic study of the conversion of UO_2 to UN by reactions involving carbon was carried out at ORNL by calculations with published free-energy data.[28] The equilibrium yields of UN per mole of nitrogen were calculated for the following reaction, using each of the gas compositions, undiluted nitrogen, nitrogen mixed with hydrogen, and nitrogen mixed with an inert diluent gas:

$$UO_2 + 2C + \tfrac{1}{2}N_2 \rightarrow UN + 2CO$$

The calculations showed that side reactions such as the formation of NH_3 or UC would have a negligible effect at equilibrium, and hydrogen was shown to act as an inert diluent. The yield of UN per mole of nitrogen gas equilibrated with UO_2–carbon mixtures was calculated to increase with temperature and with the proportion of hydrogen or inert gas mixed with the nitrogen at a total gas pressure of 1 atm, as shown in Fig. V-5.

Two methods for the above type of conversion are being investigated experimentally at ORNL.[29] For both methods the objective is to convert UO_2–carbon microspheres obtained by the sol-gel process to dense microspheres of UN. A general description of the sol-gel pro-

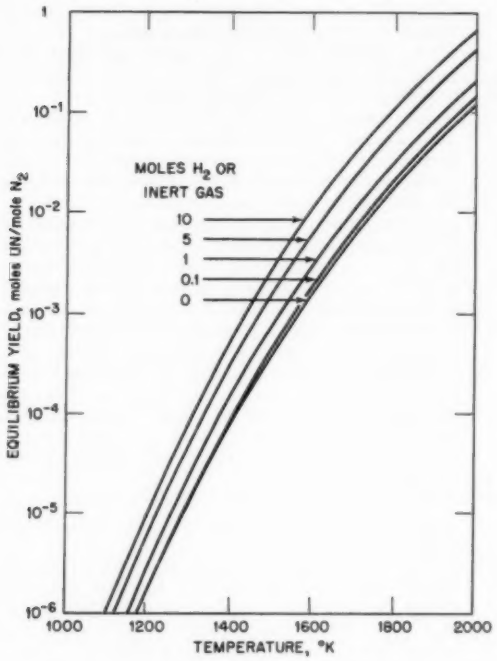

Fig. V-5 Calculated yield of uranium nitride per mole of nitrogen equilibrated with UO_2–carbon mixtures at 1 atm total pressure.[28]

cess for making ceramic microspheres was given in a previous issue of *Reactor Fuel Processing*.[30] In recent experiments, UO_2–carbon sol dispersions containing 0.58*M* UO_2 and having a carbon-to-uranium atom ratio of 2.3 to 2.7 were prepared with a sonifier. The UO_2–carbon gel microspheres were formed in a 2-in.-diameter forming column when the sol was dispersed in a forming medium of 94.5 vol.% 2-ethyl-1-hexanol, 5 vol.% 2-octanol, and 0.5 vol.% Amine-O mixture. Rigid gel spheres of about 300 μ in diameter were formed and partially dehydrated by the forming medium. The product was then dried for 16 hr at 120°C in flowing argon.

In the first method of conversion, the UO_2–carbon microspheres were reacted directly with nitrogen at 1500 to 1600°C. However, it was found that a thin coating of UN formed on the surface and prevented entry of nitrogen to the interior. This problem was avoided when the reacting spheres were cooled to 950°C after 2 hr at 1600°C in order to form higher nitrides and break up the dense coating. After the temperature was maintained at 950°C overnight, the temperature was increased to 1600°C for 3 hr. The product for which the reaction was the most complete of those reported was found to be $UN_{0.92}C_{0.13}$. The analyzed amounts of uranium, nitrogen, and carbon accounted for 99.9 wt.% of the product. The presence of the carbon was attributed to the excess amount added to the original sol. The density of the UN microsphere product, measured by toluene displacement, was 13.66 g/cm^3. This value is more than 95% of the theoretical density of 14.31 g/cm^3.

In the second method of conversion, the UO_2–carbon microspheres were first converted to UC and then to UN by the following reactions:

$$UO_2 + 3C \rightarrow UC + 2CO$$

$$UC + \tfrac{1}{2}N_2 \rightarrow UN + C$$

A preliminary experiment has been performed in which the UO_2–carbon microspheres were heated in argon for 2 hr at 1500°C to form the carbide and then for 2 more hours in nitrogen to form the nitride. The product was found to be $UN_{0.81}C_{0.40}O_{0.24}$. Since carbon is a reaction product in the second method, it was concluded that work is needed to investigate the removal of carbon by some method such as reaction with hydrogen at 1000°C. (This method of removing excess carbon from UC was reported in the Winter 1965–1966 issue of *Reactor Fuel Processing*,[31] and a complete discussion of the same work is now more readily available.[32])

The rate of self-diffusion of nitrogen in UN is an important factor in the preparation of UN, as noted above. Nitrogen diffusion rates have been measured by a method that employed ^{15}N as a tracer atom.[33] Diffusion rates were determined by observation of the rate of change of the ^{15}N partial pressure in an isotopically enriched nitrogen atmosphere over UN particles. The UN particles, measuring 190 to 337 μ, were formed by the usual hydriding–nitriding synthesis technique, followed by pressing, sintering, crushing, and sizing. The initial ^{15}N content of the circulated nitrogen atmosphere was 20 at.%. A least-squares fit to the data for several particle sizes and at temperatures between 1500 and 1900°C resulted in the following expression for the diffusion coefficient:

$$D = 2.6 \times 10^{-4} \exp(-55{,}000/RT) \quad \text{cm}^2/\text{sec}$$

Experimentation with particles of different grain sizes indicated that grain-boundary diffusion enhances the total diffusion rate at temperatures from 1500 down to 1250°C, the lowest tempera-

ture used in these experiments. Consequently the diffusion coefficients obtained for the range 1250 to 1500°C were somewhat larger than would be obtained from the above relation.

A new determination of the nitrogen pressure in equilibrium with UN was obtained by the effusion technique[34] over the temperature range 1645 to 1992°C. A least-squares fit of the data is given by

$$\log P_{N_2}\ (\text{atm}) = 8.279 - 2.874 \times 10^4\ T^{-1}\ (T \text{ in } °K)$$

An extensive study of the properties of PuN is under way at Battelle Memorial Institute.[35-39] Workers prepared most of the PuN used in these experiments by hydriding plutonium metal and reacting the resulting hydride with nitrogen at 1 atm pressure and 600°C. The hydriding characteristics of the plutonium varied and resulted in a variation in particle size. The PuN formed from the larger particles was often substoichiometric though monophasic.

Attempts to synthesize PuN by arc-melting plutonium metal in nitrogen and helium–nitrogen mixtures at 10 to 25 in. Hg pressure were unsuccessful, probably because the decomposition pressure of PuN is in excess of 25 atm at the melting point.[35]

Atmospheric corrosion of powdered PuN is severe, but, in the case of dense bodies of PuN, it is moderate.[35-38] Minus 80-mesh PuN powder was converted to oxide in one to three days by reaction with air at room temperature; after 30 days in nitrogen–1 vol.% oxygen, it contained 2.25 wt.% oxygen. Dense PuN showed a weight gain of 0.309% in 30 days when exposed to air and 0.179% in 30 days when exposed to nitrogen–1 vol.% oxygen. At 540°C, dense PuN was oxidized in dry air in 1 hr to a fine powder containing 57 wt.% of minus 325-mesh particles.[36,37] At 1000°C the oxidation was very rapid (although ignition did not take place) with the formation of a somewhat coarser powder.[36,37] Oxidation also occurred when PuN was exposed to CO_2 (Ref. 37), impure nitrogen,[37] and helium (AEC grade)[38] at elevated temperatures. However, surface passivation of a PuN specimen exposed to impure nitrogen at 900 to 1100°C appeared to occur.[37]

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Section

VI

Reactor Fuel Processing

Safety in Chemical Processing

By J. J. Barghusen and A. A. Jonke

Compatibility Studies of Anion-Exchange Resins

During the past several years, three instances of pressurization and fires have occurred in anion-exchange facilities used in the purification of plutonium from nitric acid solutions.[1,2] The significance of these events was the realization that anion-exchange resins are capable of undergoing rapid decomposition with the evolution of gases under a variety of conditions.

Van Slyke, Jansen, and Swift at the Pacific Northwest Laboratory have reported[3] the results of an investigation of the thermal behavior of anion-exchange resin (Permutit SK 20-50) in nitric acid systems, with specific emphasis on defining the cause of the incident that occurred in the Redox plant of the Hanford Atomic Products Operation[1] and establishing practical safety measures for operation of anion-exchange facilities. In the course of this study, experiments were performed using both static and dynamic systems. Static tests were performed in a 4-in.-diameter schedule-40 pipe, 4 ft long, to determine how external heat might initiate an exothermic reaction involving anion-exchange resin, equilibrated with nitric acid, contained within the vessel. The pressure vessel was equipped with a rupture-disk flange. Figure VI-1 illustrates the thermal behavior for a typical experiment that resulted in a rapid increase in internal pressure and rupture of the 300-psig pressure-relief disks. The centerline temperature of the resin exceeded the wall temperature after 1.5 hr because of internal heat generated by resin decomposition at a rate greater than the rate of heat removal through the vessel wall. The gas and steam pressure generated by the exothermic reaction finally burst the rupture disk.

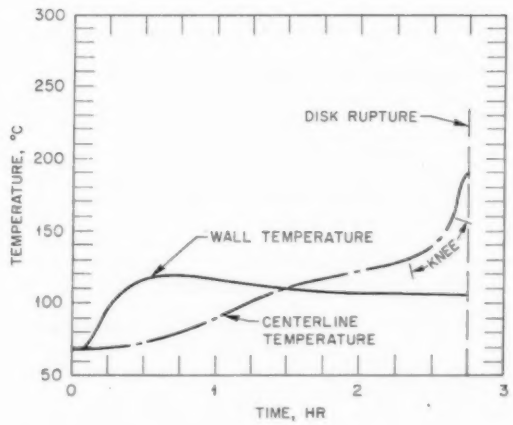

Fig. VI-1 Typical temperature behavior in resin column heated by an external heater.[3]

In a test performed with resin equilibrated with 1.9 g of sodium dichromate per liter in 7*M* nitric acid, an exothermic reaction was observed at a centerline temperature of 143°C, and the 300-psig rupture disk burst when the centerline temperature reached 160°C. It was observed after the test that the stainless-steel resin support screen was severely darkened. This effect was attributed to contact of the screen with nitric acid and dichromate solution rather than exposure of the screen to high temperatures as assumed previously.[1]

Observations made during the static tests[3] lead to the following general conclusions:

1. The reaction of the anion-exchange resin in 7*M* nitric acid shows a strong exponential temperature dependency.

2. A vessel wall temperature of 120°C is sufficient to initiate a rapid exothermic reaction in a 4-in.-diameter resin-filled pipe. However, a vessel-wall temperature of 100°C will not cause a chemical excursion.

3. Thorium-loaded resin exhibits a rate-of-temperature-rise curve that duplicates the unloaded resin curve within experimental accuracy.

4. A rapid pressure release abruptly lowers the temperature of moist resin to the atmospheric boiling temperature of the solution and effectively quenches the exothermic reaction. This "safe" pressure-release point can be as high as 200 psig.

A series of tests was performed to simulate the behavior of the Redox-plant contactor in an effort to determine how a packed bed of resin with liquid flow could produce temperatures of 120 to 130°C, leading to still higher temperatures and self-pressurization.[3] Experiments were done in a 4-in.-diameter Pyrex-glass contactor, 6 ft long, equipped with inlet, outlet, and five equally spaced centerline thermocouples. The experimental procedure involved passing a liquid feed containing 7*M* nitric acid and 1.7 g of sodium dichromate per liter through the resin column and observing the temperature at the several locations during the feeding period and after the flow had stopped. (Dichromate was added to the nitric acid feed since dichromate was present in the anion-exchange resin at the time of the incident in the Redox plant.[1]) The curves in Fig. VI-2 represent the temperature profile along the bed after the nitric acid–sodium dichromate feed had continued for 29 min and after the flow had been stopped for 5 min. The temperature of the feed solution was 55°C. The highest heat-generation rate was observed at a location 1 ft down the bed after the flow had stopped. This location

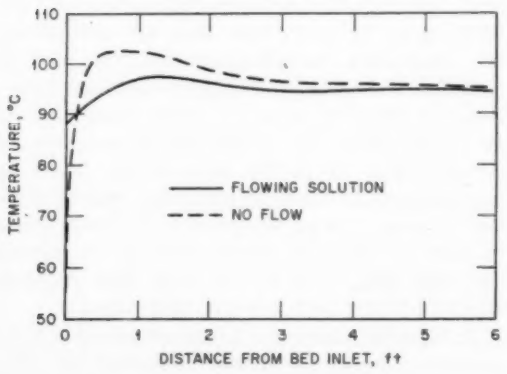

Fig. VI-2 Temperature-length profiles for flow experiment.[3]

was associated with a high loading of chromium on the resin.

An experiment was performed[3] to demonstrate the possibility of bridging the gap between the 87°C Redox contactor inlet temperature[1] and the higher temperatures needed to cause a self-sustaining exothermic reaction. The 6-ft resin bed was partially loaded with chromium from a solution containing 7*M* nitric acid and 1.8 g Cr(VI)/liter at 22°C. After 160 liters of the solution passed through the bed (feed rate, 0.87 liter/min), the feed was changed to 7*M* nitric acid at 1.1 liters/min and 80°C. Figure VI-3 illustrates the magnitude of the heating effect soon after hot-acid flow started.

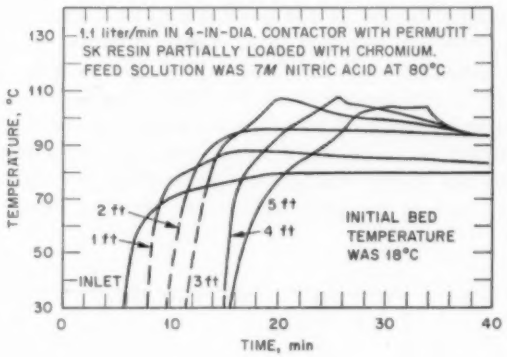

Fig. VI-3 Temperature behavior in flow experiment with chromium-loaded resin.[3]

It is evident that critical temperatures sufficient to initiate a self-sustaining exothermic reaction could have been reached if a few more feet of Cr(VI)-loaded resin bed had been present.

Calorimetric measurements have confirmed the exothermic nature of the reaction of 7*M* HNO_3 with chromium-bearing resin. A value of about 400 cal/(cm^3 of resin) per gram of Cr(VI)/(cm^3 of resin) was measured.

The high internal pressures created in the Redox anion-exchange contactor during the incident were undoubtedly caused by a runaway exothermic gas-producing reaction. The reaction must have been forced into an unstable state by either an external heat source or an abnormal exothermic chemical reaction in the resin bed.

If the incident was triggered by an external heat source, theoretical calculations have shown that the event could have been produced by an

ambient temperature of 110°C for 40 to 100 min or by an ambient temperature of 130°C for only 12 to 50 min. These temperatures could easily have been reached as a result of a small fire within an enclosed hood.

Most of the evidence suggested that the contactor pressurization preceded the fire and that an internal reaction caused the pressurization. This reasoning is supported by the presence of dichromate ion in the contactor feed. Also, it is improbable that an accidental fire would occur simultaneously with the accidental introduction of a strong oxidizing chemical like dichromate ion.

Theoretical calculations have shown that average dichromate loadings, as chromium, on the resin would have to reach at least 0.05 g/cm^3 at inlet temperatures in excess of 92°C to cause a runaway reaction (Fig. VI-4). However, at a chromium concentration of 0.3 g/cm^3 with a 70°C inlet temperature, reaction initiation would occur after a 23-min liquid-holdup time. Holdup times prior to the incident were about 22 min in the Redox contactor scrub section and about 11 min in the feed (extraction) section. Resin analyses following the Redox incident indicated that the spot chromium concentration reached at least 0.33 g/cm^3. This chromium concentration would cause pressurization at about 5.2 min with the recorded 87°C feed inlet temperature. The presence of plutonium on the resin may have further lowered the critical operating temperature.

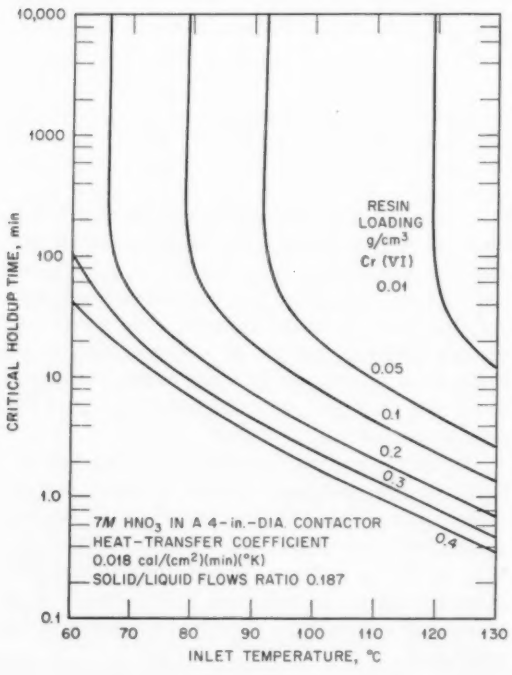

Fig. VI-4 Critical holdup time as a function of resin Cr(VI) loading and inlet temperature.[3]

Van Slyke, Jansen, and Swift[3] have correlated the chemical and physical properties of the anion resin–nitric acid system by mathematical models for batch and flow cases to predict the conditions that permit self-accelerating chemical reactions. Uncontrolled reaction is favored by: greater vessel radius, low vessel-wall heat-transfer coefficients to the surroundings, low thermal conductivity of the vessel contents, high ambient and operating temperatures, and the presence of Cr(VI) on the resin.

Several recommendations have been made which should be considered in the operation of anion-exchange contactors for plutonium service.[3] A water-jacketed contactor (high wall heat-transfer rate) may be helpful in some applications where large diameters and moderately elevated temperatures are necessary. A well-designed water jacket will also guarantee closer process temperature control than is realized in present contactors. At the other extreme, perfectly insulated, stagnant contactors are inherently unsafe, eventually pressurizing at some finite storage time if the reactant is not used up.

Strong oxidizing agents or oxidation catalysts should be avoided in organic ion-exchange-resin applications. Dichromate ion, in particular, even at low temperatures, rapidly degrades organic resins with the evolution of heat. Although the heat-generation rate in strong HNO_3 alone is much less than for dichromate at comparable temperatures, the storage of resin in strong HNO_3 should be avoided wherever possible. The storage of the resin in water or dilute HNO_3 is preferred. Conversion of nitrate-form resins to safe forms (such as the chloride form) before storage would lessen the hazards if high temperatures should occur because of external heating. Storage containers and idle contactors should have their contents vented and the resin covered with solution.

A runaway reaction in moist resin can be instantly quenched if the container or contactor is vented at relatively low pressures (200 psig or less). Evaporation provides the

cooling and quenching effect if the resin is moist. Pressure-relief valves set at lower pressures (e.g., 50 psig) would safely replace the rupture disk used in the tests reported here. Dry nitrate-form resin is inflammable and potentially explosive, and reaction quenching of dry resin cannot be achieved by pressure relief.

Gas accumulations in operating contactor resin beds have little effect on operating safety. Large discrete gas pockets are short-lived in operating contactors, and small bubble accumulations in resin beds do not significantly change the safe operating limits. Large discrete gas pockets could not affect the thermal conductivity of the bed enough to cause a self-accelerating reaction unless the contactor was already operating dangerously near the critical conditions. Gas accumulations should be avoided, not because of thermal effects, but because they can produce channeling of the process streams through the packed bed with resultant lowered operating efficiency and product purity.

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